Geochemistry of fluid discharges from Peteroa volcano (Argentina-Chile) in 2010–2015: Insights into compositional changes related to the fluid source region(s)

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Abstract

This study presents the first geochemical data of fluid discharges collected from February 2010 to March 2015 from the Planchón–Peteroa–Azufre Volcanic Complex (PPAVC), located in the Transitional Southern Volcanic Zone (TSVZ) at the border between Argentina and Chile. During the study period, from January 2010 to July 2011, Peteroa volcano experienced phreatic to phreatomagmatic eruption possibly related to the devastating Maule earthquake occurred on February 27, 2010. The compositional dataset includes low temperature (from 43.2 to 102 °C) gas discharges from (i) the summit of Peteroa volcano and (ii) the SE flank of Azufre volcano, both marked by a significant magmatic fluid contribution, as well as bubbling gases located at the foothill of the Peteroa volcanic edifice, which showed a chemical signature typical of hydrothermal fluids. In 2012, strong compositional changes affected the Peteroa gases from the summit area: the acidic gas species, especially SO2, increased, suggesting an input of fluids from magma degassing. Nevertheless, the R/Ra and δ13C-CO2 values decreased, which would imply an enhanced contribution from a meteoric-hydrothermal source. In 2014–2015, the chemical and isotopic compositions of the 2010–2011 gases were partially restored. The anomalous decoupling between the chemical and the isotopic parameters was tentatively interpreted as produced by degassing activity from a small batch of dacitic magma that in 2012 masked the compositional signature of the magmatic fluids released from a basaltic magma that dominated the gas chemistry in 2010–2011. This explanation reliably justifies the observed geochemical data, although the mechanisms leading to the change in time of the dominating magmatic fluid source are not clear. At this regard, a geophysical survey able to provide information on the location of the two magma batches could be useful to clarify the possible relationships between the compositional changes that affected the Peteroa fluid discharges and the 2010–2011 eruptive activity.

1. Introduction

Peteroa (35.240°S, 70.570°W, 3603 m a.s.l.), a composite stratovolcano belonging to the Transitional Southern Volcanic Zone (TSVZ) at the border between Argentina and Chile (e.g., Stern et al., 1984; Hildred and Moorbath, 1988) (Fig. 1), is part of the NNE-oriented Planchón–Peteroa–Azufre Volcanic Complex (PPAVC) (Tormey et al., 1995; Naranjo et al., 1999). The Peteroa summit is characterized by an −5 km wide caldera, partially covered by glaciers. It consists of four craters hosting acidic lakes and one scoria cinder cone (Fig. 2) (Tormey, 2010). The last eruptive episode of Peteroa lasted from January 2010 up to July 2011 and was characterized by phreatic and phreatomagmatic eruptions with a VEI ≤2 (Haller and Risso, 2011; Aguiler et al., 2012; Naranjo, 2012). It is worth noting that the
devastating February 27, 2010 Maule earthquake (Mw 8.8) that affected central-southern Chile (Jara-Muñoz et al., 2015 and references therein) was concomitant with the Peteroa volcanic activity. After this seismic event up to 2011, PPAVC suffered several Mw < 3 seismic events (up to 15 km depth) (SERNAGEOMIN-OVDAS, 2010a,b,c, 2011a,b), probably related to the co-seismic release of fluids from a hydrothermal reservoir (Pritchard et al., 2013). The latter likely caused the emission of volcanic plumes from craters #2 and #3 (Fig. 2) during the last eruptive episode (Aguilera et al., 2012; Naranjo, 2012).

In this study, we present the chemical and isotopic (δ18O–H2O, δδ–H2O, δ13C–CO2, 3He/4He, 40Ar/36Ar and δ15N–N2) compositions of gases sampled during the five sampling campaigns (February 2010, March 2011, March 2012, March 2014 and March 2015) from i) fluid discharges located at the Peteroa summit and along the SE flank of the Azufe volcano and ii) thermal bubbling pools situated at the base of the E and SE flanks of PPAVC (Fig. 2). Chemical data of water samples collected from the lakes hosted within craters #1, #2 and #4 (Fig. 2) were also reported. The main aim was to investigate the fluid source regions and the physical–chemical processes controlling the chemistry of the Peteroa gases in 2010–2015, highlighting the temporal compositional variations and their possible relationship with the 2010–2011 eruptive activity. To the best of our knowledge, this is the first geochemical survey carried out on fluids discharged from this volcano.

2. Geological and volcanological setting

The Pleistocene–Holocene PPAVC lies on Upper Jurassic to Cretaceous continental and marine sediments (limestone, conglomerates, sandstones and gypsum sequences), pyroclastic rocks, and basaltic to rhyolitic lava flows which are locally intruded by Middle Tertiary dextral to granodioritic plutons (Tormey et al., 1989, 1995; Naranjo et al., 1999; Naranjo and Haller, 2002). These rock formations are variably folded and thrusted, given the occurrence of NNE-oriented reverse faults pertaining to the Malargüe fold-and-thrust belt (Giambiagi et al., 2003).

The spatial orientation of PPAVC, as well as the location of the thermal manifestations (e.g., hot springs, bubbling pools, mud pools, fumaroles, steaming grounds) recognized N, E and SE of the volcanic complex, is controlled by the occurrence of these reverse faults (Cembrano and Lara, 2009; Gutierrez et al., 2012). At a regional scale, the volcanic activity in the TSVZ area is related to the subduction of the Nazca beneath the South American plates (Barazangi and Isacks, 1976; Cande and Leslie, 1986, 1987). Azufe volcano is the oldest (<1.20 My) and largest (~69 km3) edifice of PPAVC, consisting of basaltic andesite lava and pyroclastic flows, dacitic lava flows and domes, and lahars deposits. Planchón volcano (6 km north of the Azufe cone) was built in 3 different phases: i) Planchón I (from ~14 to ~12 ky), with basaltic and basaltic andesite lava flows, pyroclastic deposits and minor lahars deposits having a total volume of ~43 km3; ii) Planchón–Teno (~12 ky), an ~10 km3 debris avalanche deposit produced by the collapse of the western flank of Planchón I (Hauser 1990, 1993); iii) Planchón II (from ~12 to ~7 ky), consisting of basaltic to basaltic andesite lava flows and pyroclastic sequences, and lahars deposits whose total volume is ~5 km3. Peteroa volcano is the smallest (~1 km3) and youngest (~<7 ky) edifice. Its activity is characterized by basaltic andesite to andesitic lava flows and basaltic andesite to dacitic pyroclastic flows, surge and fall deposits. According to Tormey et al. (1995), the volcanic products of PPAVC evolved from basalts and, secondarily, dacites (Azufe–Planchón) sourced from relatively moderate-pressure (~4 to 8 kbar), to andesite (Peteroa), produced by magma mixing processes at relatively shallow depth. NNE-oriented reverse faults, developed in a compressive regime caused by the Malargüe fold and thrust belt (Ramos et al. 2004), controlled the spatial orientation of PPAVC (Cembrano and Lara, 2009), as well as the location of the thermal manifestations (e.g., hot springs, bubbling pools, mud pools, fumaroles, steaming grounds) recognized at N, E and SE of the volcanic complex (Gutierrez et al., 2012).

Fifteen glaciers, whose size significantly reduced in the last years and currently occupying a surface of ~20 km2, occur at the PPAVC summit and its surroundings (Liaudat et al., 2014).
3. Historical eruptive activity

Peteroa is the only volcano of PPAVC that has experienced historical eruptive activity, during which phreatic and phreatomagmatic events ($\text{VEI} \leq 3$) occurred (1660, November–December 1751, March 1762, 1835, February 1837, 1842, 1860, 1869, 1872, 1878, 1889–1894, 1938, November 1959, August 1960, January 1962, February 1967, February 1991 and November 1998) (Gonzalez-Ferrán, 1995; Naranjo et al., 1999; Naranjo and Haller, 2002). The last eruptive activity from crater #3 (Fig. 2), from January 2010 to July 2011, consisted of four stages, as follows:

Stage 1 (from 4th January to 8th August 2010): Emission of a 100–200 m high white (gas and vapor) plume possibly related to the occurrence of phreatic explosions in the SW side of crater #3.
Stage 2 (from 4th September to 1st November 2010): Emission of a plume having a maximum height of ~3 km that was visible up to 345 km toward ESE. Ash fall deposits covered an area of 1265 km$^2$.
Stage 3 (from 17th February to 20th May 2011): Emission of a white ESE-oriented plume (up to ~1000 m above the crater rim). Tephra deposits consist of poorly vesicular andesitic fragments of lava, glassy lava, quartz, plagioclase and pyroxene crystals with no evidence of hydrothermal alteration (Aguilera et al., 2012).
Stage 4 (from 17th June to 13th July 2011): Sporadic explosions produced a 500–2000 m high, SE-oriented intermittent plume.

The epicenters of the seismic activity recorded during the 2010–2011 eruptive activity were located in two main zones, 16–33 km NE and 5–7 km N from active crater, with focus located at 1–30 km and 1–8 km depth, respectively (SERNAGEOMIN-OVDAS, 2010a, b, 2011a, b). A third epicenter zone, 9–20 km SE from the active craters and with focus at 1–15 km depth, was recognized. Most earthquakes

Fig. 2. Satellite image of the Planchón–Peteroa–Azufre Volcanic Complex (PPAVC). Crater zone at Peteroa volcano, fumarolic fields, crater lakes, thermal springs and location of the sampling sites are shown. Filled squares: gas sample; half-filled square: gas and water sample; open square: water sample. Red star corresponds to the soil and air temperature monitoring site of Liaudat et al. (2014).
(>85%) were interpreted as produced by rock fracturing, whereas few of them were related to underground fluid circulation (SERNAGEOMIN-OVDAS, 2010a,b,c, 2011a,b).

4. Material and methods

4.1. Gas and water sampling

Gas samples were collected from different zones (Fig. 2), as follows: (1) between craters #2 and #3 (Pet1, Pet2, Pet7 and PetB); (2) the bottom of crater #2 (Pet3, Pet4, Pet5 and Pet6); (3) the SE flank of the Azufre volcano (Azf1 and Azf2); (4) the Valenzuela valley (Azf2); (5) the Glacial valley (Gen1 and Gen2); (6) the Los Azufres valley (EM, Cur, Pel and Per). Gases from the fluid emissions were conveyed into glass flasks using a 1 m long titanium tube (Ø = 2.5 cm) that was inserted into the gas vent and connected through glass-dewared tubes to the sampling flasks. A plastic funnel upside-down submerged in the pools and connected to the sampling flasks through tygon tubes was used to sample the bubbling gases. Sampling flasks used to collect gases from both the discharges of the volcano summit and the bubbling pools consisted of pre-evacuated 60 mL glass thorium-tapped flask filled with 20 mL of 4 N NaOH and 0.15 M Cd(OH)2 suspension (Montegrossi et al., 2001). During sampling, water vapor and acidic gases (CO2, SO2, HCl and HF) dissolved in the alkaline solution, whereas H2S formed insoluble CdS. Low-solubility gas species (N2, O2, CO, H2, He, Ar, Ne, CH4 and light hydrocarbons) were concentrated in the sampling flask headspace.

Aliquots of vapor condensates (for the analysis of δ13O and δ18O in water vapor) and dry gases (for the analysis of CO and 13C/12C ratio in CO2) were sampled using an ice-cooled glass tube connected to the gas sampling line (Montegrossi et al., 2001; Vaselli et al., 2006). In 2012, six gas samples were collected in 100 mL sampling flasks filled with 50 mL of 4 N NaOH for the analysis of δ18O.

In 2011, three water samples from the crater lakes hosted in craters #1 (Pet10), #2 (Pet5) and #4 (Pet9) (Fig. 2) were collected in 200 mL sterile polyethylene bottles, after filtering at 0.45 μm. Not filtered water was collected in 100 mL dark glass bottles for the analysis of δ18O and δD. Using this sampling method, one water sample from the lake hosted in crater #2 (Pet5) was also collected in 2012. In 2011 and 2012, water aliquots from the pools where the bubbling gases were collected (Pet, Gen and Cur) were also sampled for the analysis of δ18O and δD.

4.2. Chemical and isotopic (R/Ra, δ13C–CO2, 40Ar/36Ar and δ15N) analysis of gases and steam (δ18O and δD)

Inorganic gases (N2, Ar + O2, H2, He and CO) in the flash headspace of samples collected in 2010, 2011, 2014 and 2015 were analyzed at the Department of Earth Sciences of the University of Florence (Italy) using a Shimadzu 15A gas chromatograph (GC) equipped with a 10 m long 5Å molecular sieve column and a thermal conductivity detector (TCD). Argon and O2 were analyzed using a Thermo Gas chromatograph equipped with a 10 m long capillary molecular sieve column and a TCD. A Shimadzu 14A gas chromatograph (GC) equipped with a 10-m-long stainless steel column packed with Chromosorb PAW 80/100 mesh coated with 23% SP-1700 and a flame ionization detector (FID) was used to analyze CH4 and light hydrocarbons. The liquid and the solid precipitate in the alkaline suspension were separated by centrifugation at 4000 rpm for 30 min. The liquid phase was used to analyze 1) CO2, as CO2−, by automatic titration (AT; Metrohm Basic Titrisal) with a 0.5 N HCl solution; 2) HCl, as Cl−, by ion chromatography (IC; Metrohm 761); 3) SO2 as SO42−, after oxidation with 5 mL H2O2 (33%) by IC. Using 5 mL H2O2 (33%), CdS in the solid precipitate was oxidized to SO42− that was analyzed by IC for determining H2S concentrations (Montegrossi et al., 2001). HF concentrations were calculated on the basis of F− concentrations in the condensates. The analytical errors for AT, GC and IC analyses were <5%.

The analysis of 13C/12C of CO2 (δ13C–CO2, expressed as ‰ vs. V-PDB) of the 2010, 2011, 2014 and 2015 samples were carried out with a Finnigan Delta S mass spectrometer after standard extraction and purification procedures of the gas mixtures (Evans et al., 1998; Vaselli et al., 2006). Standards used for estimation of external precision were Carrara and San Vincenzo marbles (Internal), NBS18 and NBS19 (International), whereas the analytical error and the reproducibility were ±0.05‰ and ±1.0%, respectively. The δ13C–CO2 values of the 2012 samples were carried out following chromatographic separation using GB1. The analytical error was ±0.06‰.

The He isotopic ratios (expressed as R/Ra, where R is the 3He/4He measured ratio and Ra is the 3He/4He ratio in the air: 1.39 × 10−6; Mamyrin and Tolstikhin, 1984) were determined at the INGV laboratories of Palermo (Italy) on gas aliquots transferred from the flask headspace into pre-evacuated 50 mL flasks. After standard purification procedures, Ne was cryogenically separated from He at 77 K by absorption in a charcoal trap cooled at 12 K. The abundances and isotope compositions of He, as well as the 3He/4He/Ne ratios, were then determined by separately admitting He and Ne into a split flow tube mass spectrometer (Helix SFT). The analytical error was ≤0.3‰ (Paonita et al., 2013). The measured R/Ra values were corrected for atmospheric contamination using the 4He/36Ne ratios (Pureda and Craig, 1989), as follows:

\[
R/\text{Ra} = \left( [\text{R}/\text{Ra}_{\text{meas}}]−1 \right)/(1−r)
\]

where \( r \) is \( [\text{4He}/\text{36Ne}]_{\text{air}}/[\text{4He}/\text{36Ne}]_{\text{meas}} \) (0.318; Ozima and Posdeek, 1983).

The chemical composition and the δ15N (expressed as ‰ vs. air) and 40Ar/36Ar ratios in the 2012 gas samples were determined at the INGV laboratories of Naples (Italy) using an Agilent 6890N gas chromatograph (GC) coupled with a Finnigan Delta plusXP continuous-flow mass spectrometer (MS). The GC was equipped with a molecular sieve column (MS 5 Å capillary, 30 m × 0.53 mm × 50 μm; He carrier gas), TCD detector and a post column switching device (Denswitch) that had the following function: i) to split the column gas flow to the TCD detector and to the MS, and ii) to invert the column flow after the species of interest (Ar and N2) had reached the detector, preventing undesirable species (mainly CO and water) from reaching the MS. To allow simultaneous determination of 40Ar and 15N, the MS was equipped with a standard triple collector. Initially, the ion beam was focused to send mass 36 to the more sensitive cup. After recording the mass 36 peak, the magnetic field was switched to focus the ion beams of masses 28, 29 and 30 on the three cups using a jump calibration procedure taking into account any hysteresis of the magnet. Analytical errors were: δ15N ± 0.1‰, 36Ar < 1‰, 40Ar < 3‰.

The δ18O/δD and δ3/H isotopic ratios (δ18O–H2O and δD–H2O, expressed as ‰ vs. V-SMOW) of the condensates and water samples were determined using a Finnigan Delta Plus XL mass spectrometer at the Geokarst Engineering Laboratory (Trieste, Italy). Oxygen isotopes were analyzed following the method described by Epstein and Mayeda (1953). Hydrogen isotopes were analyzed on H2 generated by the reaction of 10 μL water with metallic zinc at 500 °C, according to the analytical procedure described by Coleman et al. (1982). The analytical errors were ±0.1% for δ18O and ±0.1% for δD, using V-SMOW and SLAP as analytical standards and AR-1 as an internal standard. The δ18O–H2O and δD–H2O values of the 2012 gas samples were analyzed at the INGV laboratories of Naples (Italy) using a Finnigan Delta plusXP continuous-flow mass spectrometer (MS) coupled with a Gasbench gas-chromatographic device (GB1), using equilibration techniques with CO2 for oxygen (Epstein and Mayeda, 1953), and with H2 for hydrogen (Nelson, 2000). The analytical errors were ±0.08‰, and ±1‰ for δD and δ18O, respectively.
Table 1
Type, date, geographical coordinates (UTM, WGS 85 Zone 19), altitude (m a.s.l.), outlet temperatures (°C), chemical composition (dry gas fraction) of inorganic gases and CH₄ (in mmol/mol), and total concentration of the dry gas fraction (Xg in %) for the PPAVC gas discharges.

| ID | type       | date        | latitude  | longitude  | altitude | outlet temperatures (°C) | chemical composition (dry gas fraction) of inorganic gases and CH₄ (in mmol/mol) | total concentration of the dry gas fraction (Xg in %) |
|----|------------|-------------|-----------|------------|----------|--------------------------|-------------------------------------------------------------------------------------|-----------------------------------------------------|
|    |            |             |           |            |          | T | CO₂ | HCl | HF | SO₂ | H₂S | N₂ | CH₄ | Ar | O₂ | H₂ | He | CO |    |
| Pet1 | Fumarole | February 2010 | 357027   | 3436      | 3436     | 91.8 | 978 | 0.25 | 0.011 | 0.12 | 19 | 1.6 | 0.24 | 0.026 | 0.056 | 0.36 | 0.0032 | 0.0026 | 9.5 |
| Pet2 | Fumarole | February 2010 | 356908   | 3434      | 102      | 961 | 0.19 | 0.021 | 0.17 | 35 | 2.7 | 0.29 | 0.024 | 0.049 | 0.38 | 0.0028 | 0.0031 | 8.9 |
| Pet3 | Fumarole | March 2011   | 357027   | 3436      | 87.7     | 975 | 0.37 | 0.010 | 0.055 | 21 | 2.6 | 0.13 | 0.0043 | 0.0065 | 0.25 | 0.0014 | 0.015 | 14.6 |
| Pet4 | Fumarole | March 2011   | 357037   | 3374      | 88.4     | 979 | 0.38 | 0.012 | 0.051 | 18 | 2.3 | 0.098 | 0.0016 | 0.0047 | 0.21 | 0.0012 | 0.0092 | 12.1 |
| Pet5 | Fumarole | March 2011   | 357171   | 3358      | 87.9     | 978 | 0.31 | 0.010 | 0.041 | 19 | 2.4 | 0.10 | 0.0047 | 0.0068 | 0.23 | 0.0015 | 0.015 | 15.0 |
| Pet6 | Fumarole | March 2011   | 356939   | 3411      | 88.3     | 980 | 0.38 | 0.011 | 0.054 | 16 | 2.3 | 0.091 | 0.0043 | 0.010 | 0.28 | 0.0022 | 0.012 | 15.4 |
| Pet7 | Fumarole | March 2012   | 357027   | 3436      | 87.8     | 382 | 1.3  | 14 | 4.48 | 145 | 9.5 | 0.014 | 0.025 | 0.0004 | 0.32 | 0.0037 | 0.0012 | 3.4 |
| Pet8 | Fumarole | March 2012   | 357037   | 3374      | 89.4     | 380 | 1.3  | 14 | 450 | 148 | 7.3 | 0.012 | 0.0079 | 0.0009 | 0.23 | 0.0034 | 0.0010 | 2.8 |
| Pet9 | Fumarole | March 2012   | 356939   | 3411      | 87.9     | 370 | 1.3  | 14 | 456 | 153 | 6.5 | 0.013 | 0.0047 | 0.0005 | 0.36 | 0.0036 | 0.0009 | 3.8 |
| Pet10| Fumarole  | March 2012   | 356939   | 3416      | 87.8     | 282 | 1.2  | 12 | 534 | 162 | 7.8 | 0.015 | 0.0014 | 0.0007 | 0.47 | 0.0043 | 0.0008 | 3.0 |
| Azf1 | Fumarole  | March 2012   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
| Azf2 | Fumarole  | March 2012   | 359912   | 2766      | 87.8     | 781 | 4.7  | 0.9  | 26 | 181 | 3.6 | 0.094 | 0.041 | 0.0060 | 3.1 | 0.0009 | 0.0087 | 2.56 |
| Pet7 | Fumarole  | March 2014   | 357037   | 3374      | 89.5     | 916 | 0.56 | 0.035 | 31 | 47  | 5.3 | 0.089 | 0.007 | 0.0011 | 0.41 | 0.0033 | 0.0026 | 5.8 |
| Pet11| Fumarole  | April 2015   | 357027   | 3436      | 88.1     | 958 | 0.31 | 0.016 | 1.2 | 35  | 4.9 | 0.16 | 0.0045 | 0.0039 | 0.32 | 0.0018 | 0.0074 | 11.3 |
| Azf2 | Fumarole  | March 2015   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
| Azf1 | Fumarole  | March 2015   | 359912   | 2766      | 87.8     | 781 | 4.7  | 0.9  | 26 | 181 | 3.6 | 0.094 | 0.041 | 0.0060 | 3.1 | 0.0009 | 0.0087 | 2.56 |
| Azf2 | Fumarole  | March 2015   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
| Azf1 | Fumarole  | March 2015   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
| Azf2 | Fumarole  | March 2015   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
| Azf1 | Fumarole  | March 2015   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
| Azf2 | Fumarole  | March 2015   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
| Azf1 | Fumarole  | March 2015   | 359938   | 2758      | 88.7     | 794 | 5.3  | 0.8  | 3.8 | 156 | 3.2 | 0.086 | 0.046 | 0.0011 | 0.26 | 0.0011 | 0.0069 | 3.1 |
4.3. Chemical analysis of waters

Temperature and pH of lake water were determined in the field. Water samples were analyzed for major cations (Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), and NH\(_4\)^{−}) and anions (F\(−\), Cl\(−\), SO\(_4^{2−}\), Br\(−\) and NO\(_3^{−}\)) by IC (Metrohm 861 and Metrohm 761, respectively). The analytical error was ≤5%.

5. Results

5.1. Chemical composition of gases

Location of the sampling points (UTM coordinates; WGS 84 Zone 19), altitude (m a.s.l.), outlet temperatures of the gas vents, water temperatures of the bubbling pools (°C) and chemical composition (expressed in mmol/mol) of the dry gas fraction (Xg in %) are reported in Table 1.

The gas discharges from the summit area, consisting of fumarolic-like vents whose outlet temperature ranged from 43.2 to 102 °C, were dominated by CO\(_2\) (up to 986 mmol/mol), followed by water vapor (Xg from 2.8% to 21.8%). The dry gas composition of samples collected in 2010, 2011 and 2015 from the Peteroa vents (up to 0.0032 mmol/mol), and C\(_6\)H\(_6\) (0.0025 mmol/mol), respectively. Thiophene (C\(_4\)H\(_4\)S) and furane (C\(_4\)H\(_4\)O) were also detected (Table 2).

SO\(_2\) concentration (up to 534 mmol/mol) was three orders of magnitude higher whereas those of CO\(_2\) ranged from 282 to 382 mmol/mol. Similar concentrations were also shown by the concentrations of other acidic species, i.e. H\(_2\)S, HCl and HF (up to 162, 14 and 1.3 mmol/mol, respectively), whereas N\(_2\) and H\(_2\) showed slight increases (from 6.5 and 9.5 to 0.23 to 0.47 mmol/mol, respectively). On the contrary, CH\(_4\) and CO significantly decreased, down to ≤0.015 and ≤0.0012 mmol/mol, respectively. Hydrocarbon concentrations decreased, especially the C\(_4\)-compounds and CH\(_4\) that were below the detection limit (0.0000005 mmol/mol).

In 2014, the Peterea fluid discharges showed compositional features similar to those recorded for the 2010–2011 and 2015 samples, with the exception of SO\(_2\), H\(_2\)S and N\(_2\) that were characterized by slightly higher concentrations (up to 1.6, 39 and 4.9 mmol/mol, respectively).

The composition of the fumaroles from the flanks of Azufre volcano (March 2012) partially resembles that of the gases collected from the Peterea summit in the same period, although the former had significantly higher CO\(_2\) and H\(_2\)S concentrations (up to 794 and 3.1 mmol/mol, respectively) and lower SO\(_2\) (up to 38 mmol/mol).

Gases collected from the bubbling pools in 2010, 2011, 2012 and 2015, whose temperatures ranged from 24 to 46.2 °C, were characterized by a CO\(_2\)-dominated (up to 996 mmol/mol) chemical composition, absence of acidic gases and CO, significant concentrations of N\(_2\) and CH\(_4\) (up to 8.1 and 1.8 mmol/mol, respectively), and relatively low concentrations of H\(_2\)S (≤0.0078 mmol/mol). Light hydrocarbons mostly consisted of C\(_2\)H\(_6\) (up to 0.027 mmol/mol), with minor C\(_3\)-C\(_4\) alkanes (up to 0.0035 mmol/mol), C\(_2\)H\(_6\) (up to 0.0066 mmol/mol) and C\(_3\)H\(_8\) (up to 0.0016 mmol/mol), whereas C\(_2\)H\(_6\), C\(_3\)H\(_8\) and CH\(_4\)O were not detected (Table 2). The composition of bubbling gases (Gen2, AZ and Pet) did not show significant temporal changes.

5.2. Isotopic composition of gases (Rc/Ra, δ\(^{13}\)C–CO\(_2\), 40Ar/\(^{36}\)Ar, δ\(^{15}\)N–N\(_2\)) and steam (δ\(^{18}\)O–H\(_2\)O and δd–H\(_2\)O)

The isotopic composition of water vapor (δ\(^{18}\)O–H\(_2\)O and δd–H\(_2\)O), CO\(_2\) (δ\(^{13}\)C–CO\(_2\)), He (Rc/Ra), Ar (40Ar/\(^{36}\)Ar), and N\(_2\) (δ\(^{15}\)N–N\(_2\)) in the Peterea gas samples are reported in Table 3. The δ\(^{18}\)O–H\(_2\)O and δd–H\(_2\)O values showed temporal changes.
H₂O values of the fluid discharges sampled in 2010–2011 from the Peteroa summit ranged from −5.9‰ to −3.5‰ and from −80‰ to −73‰ vs. V-SMOW, respectively, whereas those of the 2012 and 2015 gases from both the Peteroa summit and the Azufre volcano were significantly more negative, down to −17.2‰ and −119‰ vs. V-SMOW, respectively, similar to those of the waters from the bubbling pools (down to −15.1‰ and −106‰ vs. V-SMOW, respectively). The Peteroa summit gases were also affected by significant temporal changes of the δ¹³C–CO₂ values, which in 2010, 2011 and 2015 ranged from −7.6‰ to −2.02‰ vs. V-PDB, whereas in 2012 were −11.2‰ vs. V-PDB, similar to those of the Azufre fumarole (−11.9‰ vs. V-PDB) and the bubbling pools (−13.2‰ to −12.1‰ vs. V-PDB).

In 2012, the Rc/Ra values, which in 2010–2011 ranged from 6.87 to 7.11, strongly decreased (from 4.43 to 4.46), whereas afterwards they showed an opposite trend, progressively increasing up to 5.62 (2014) and 6.68 (2015). The bubbling gases showed a wide range of Rc/Ra values: from 1.19 to 5.94. The ⁴⁰Ar/³⁶Ar ratios in the gases from the Peteroa summit (up to 491) were significantly higher than that of air (295.5), whereas in the bubbling gases they ranged from 295 to 328. The δ¹⁸O values in the 2011–2012 summit discharges were in a relatively narrow range (from 4.27‰ to 5.94‰ vs. air), whereas in the Cur and Gen2 bubbling gases they were −0.34‰ and 1‰ vs. air, respectively.

5.3. Chemical and isotopic (δ¹⁸O–H₂O and δD–H₂O) compositions of crater lakes

Temperature, pH and chemical composition of the crater lakes hosted in craters #1 (Pet10), #2 (Pet5) and #4 (Pet7) (Fig. 2) are reported in Table 4. Temperature and pH ranged from 7.4 to 43.2 °C and from 1.49 to 2.91, respectively. The lake chemistry was invariably dominated by SO₄²⁻ (up to 3300 mg/L; Pet), whereas Cl⁻ concentrations ranged from 44 to 660 mg/L. The most abundant cation was Ca²⁺ (up to 520 mg/L), followed by Mg²⁺ (380 mg/L), Na⁺ (180 mg/L) and K⁺ (130 mg/L). Significant concentrations of minor species, such as F⁻, NH₄⁺, NO₃⁻ and Br⁻ (up to 38, 10, 2.0 and 1.4 mg/L, respectively), were measured. The δ¹⁸O–H₂O and δD–H₂O values ranged from −10 to −9.5‰ and from −80‰ to −74‰ vs. V-SMOW, respectively.

Table 4. Temperature (in °C), pH, chemical composition (in mg/L) and isotopic composition of waters (δ¹⁸O and δD) vs. V-SMOW) from lakes of the Peteroa summit craters.

| ID  | Crater | Date   | Latitude | Longitude | Altitude | T     | pH    | Cl⁻  | SO₄²⁻ | Na⁺  | K⁺   | Ca²⁺ | Mg²⁺ | NO₃⁻ | F⁻   | Br⁻ | NH₄⁺ | δD  | δ¹⁸O   |
|-----|--------|--------|----------|-----------|----------|-------|-------|-------|-------|------|------|------|------|------|------|-----|------|-----|--------|
| Pet5 | #5    | March 2011 | 6099157  | 357050   | 3331    | 43.2  | 1.49  | 44    | 3300  | 82   | 130  | 220  | 140  | 5.0  | 14.0 | 5.2 | 10.0 | −74 | −9.5  |
| Pet9 | #4    | March 2011 | 6095324  | 356704   | 3353    | 15.1  | 2.73  | 200   | 3000  | 180  | 42   | 330  | 380  | 1.0  | 9.9  | 0.77 | 4.9  | −80 | −9.9  |
| Pet10| #1    | March 2011 | 6098725  | 357071   | 3263    | 7.4   | 2.91  | 660   | 2000  | 140  | 34   | 520  | 180  | 1.0  | 39   | 1.4  | 2.6  | −80 | −10   |
| Pet5 | #2    | March 2012 | 6099157  | 357050   | 3331    | 30.6  | 1.50  | 92    | 2800  | 63   | 16   | 180  | 95   | 0.81 | 2.4  | 0.52 |
were significantly more negative (Table 3). Although the $\delta^{13}C$-CO$_2$ values do not provide an unambiguous parameter to distinguish between mantle and crustal CO$_2$ (Sherwood Lollar et al., 1997), these changes seem to indicate that in 2012 a significant increase of crustal-type, $^{13}C$-rich fluids occurred. The temporal evolution of the R$_c$/R$_a$ ratios, showing a significant enrichment in $^4$He in 2012 and, at a lower extent, in 2014 with respect to the values measured in 2011 and 2015, seems to support this hypothesis. On the contrary, the measured $\delta^{15}N$ values (between 4.27 and 5% vs. air.) do not allow to clearly discriminate between crustal and magmatic sources. Such a positive isotopic signature is indeed typical of 1) N$_2$ produced by thermal decomposition of organic material buried in sedimentary material (Jenden et al., 1988; Fischer et al., 2002; Snyder et al., 2003; Ingugliatto et al., 2004) likely involved in the subduction process, and/or 2) low-grade metamorphism affecting NH$_4$ fixed in the crystal lattices of K-rich minerals (micas and K-feldspars) of crystalline rocks (e.g., Honma and Ithihara, 1981; Mingram and Brauer, 2001).

Summarizing, He and Carbon (in CO$_2$) isotopic parameters consistently indicate that during the 2010–2011 eruptive activity, the Peteroa summit fluid discharges were dominated by a magmatic component that decreased in 2012 and increased again in 2014–2015. Notwithstanding, variable inputs of magmatic vs. crustal fluid contribution cannot exhaustively explain all the observed changes that affected the chemical and isotopic parameters of the Peteroa gases. According to this hypothesis, the dramatic decrease of the R$_c$/R$_a$ and $\delta^{13}C$–CO$_2$ values measured in 2012 would imply an increase of CO$_2$ and $^4$He from a crustal source. However, an enhanced crustal contribution is not consistent with both the CO$_2$/He decrease and the huge SO$_2$ increase recorded in 2012. The production of SO$_2$ from a crustal source, such as pre-existing sulfur deposits, needs a significant increase of temperature that conflicts with the flat temporal patterns of both (i) the most sensitive temperature-dependent parameters (H$_2$ and CO$_2$), and (ii) the outlet temperature and flux of the fumaroles. The 2010–2011 activity stopped before the 2012 sampling, thus the possible influence of these events on sulfur remobilization were to be expected to occur during the eruptive activity, not later. Moreover, sulfur remobilization cannot explain the increases of HCl and HF measured in 2012, as well as the synchronous strong variations of N$_2$, CH$_4$ and light hydrocarbons (Table 1).

It is worth noting that the process(es) that caused the compositional changes at the Peteroa summit seems to have affected at a minor extent the Azufe gases, since their compositions were intermediate with respect to that observed at Peteroa in 2012 and 2014–2015 (Table 1). As already mentioned, the chemical and isotopic features of the bubbling gases from the surroundings of PPAVC did not show significant temporal variations.

6.3. Magma degassing model

6.3.1. Preliminary assumptions

A tentative explanation for the appearance of the Cl- and S-rich signature in the 2012 Peteroa gas discharges could be involving a gas contribution from a magma characterized by a very advanced extent of degassing. In fact, a gas phase released from strongly degassed magma is typically enriched in species characterized by high solubility in silicate degassing. In fact, a gas phase released from strongly degassed magma is typically enriched in species characterized by high solubility in silicate melt (e.g., Cl and S). Recent works (Paonita et al., 2012, 2013; Caliro et al., 2014) have shown that ratios among inert gases and CO$_2$ can be used to recognize signatures of magma degassing and quantify the degassing degree, even in fumarolic fields where the contribution from underlying hydrothermal systems is significant. According to the relative solubility of Cl $>$ S $>$ CO$_2$ $>$ He $>$ N$_2$ in water, the N$_2$/He ratios are virtually unaffected by interaction with hydrothermal liquids even in gas phases that have suffered a complete removal of Cl and S (Liotta et al., 2010; Paonita et al., 2012). Moreover, the He/CO$_2$ and N$_2$/CO$_2$ ratios increase by no more than 30–40% when S is still present in the residual gases and Cl has completely been scrubbed (Liotta et al., 2010, Paonita et al., 2012). Hence, although the ratios of these gases were
strongly affected by scrubbing due to the hydrothermal system, they were tentatively used as indicators of magma degassing to model the compositional evolution recorded in 2010–2015 at Peteroa. In Fig. 4a, the 2010–2011 Peteroa samples outline a rough sub-vertical trend from high to low N2/He ratio (see the black arrow). Given that N2 solubility in any kind of silicate melt composition is much lower than that of He (Iacono-Marziano et al., 2010), the trend qualitatively suggests a growing extent of magma degassing. The decrease of the N2/He ratio by magma degassing seems to be paralleled by a slight decrease of N2/CO2. In contrast, the Cl- and S-richest gases collected in 2012 from the Peteroa summit displayed very high N2/CO2 ratios (Fig. 4a) with respect to those of the 2010–2011 gases, suggesting the occurrence of a process able to increase in time the N2/CO2 ratio (see gray arrow in Fig. 4a). As modeled by Caliro et al. (2014), the N2/CO2 ratio during magma degassing strongly depends on silicate melt composition, as the ratio decreases during degassing of mafic magmas while it increases for more evolved melts. Therefore, the Cl- and S-rich signature of the 2012 samples was possibly caused by degassing of a magma batch with a more evolved composition than that of 2010–2011. With the aim to quantitatively explore this hypothesis, the isothermal degassing model for H2O–CO2–N2–He–Ar mixtures by Nuccio and Paonita (2001), with the recent upgrades proposed by Caliro et al. (2014), was applied. The model computed the compositional change of the gas phase released from a magma during its progressive decompression, according to the vapor-melt partition coefficients of the involved gases.

Briefly, the adopted solubility values for H2O–CO2 mixed vapor and noble gases were from Papale et al. (2006) and from Iacono-Marziano et al. (2010) and Paonita et al. (2012), respectively. Following Caliro et al. (2014), the proposed approach was to:

1) compare the results from the Papale et al. (2006) model with the experimental data by Lesne et al. (2011) and Behrens et al. (2004) for basaltic and dacitic magmas, and properly regulate the FeO/Fe2O3 ratio of the model to fit the experimental results; 2) use Ar solubility as a proxy for predicting N2 solubility in silicate melts; 3) use the experimental relationship of He and Ar solubility versus dissolved H2O in melt found by Paonita et al. (2000, 2012) in order to compute the effects of H2O on Henry’s constant of the inert gases.

To provide a semi-quantitative interpretation of the acidic gas contents in terms of degassing processes, S was included in the Nuccio and Paonita (2001) model by following the approach of Aiuppa et al. (2004). This requires to deal with S as a minor species and to select a proper fluid-melt partition coefficient (DF-m). The value of DF-m for basalt was the pressure-dependent one (Aiuppa et al., 2004), which resulted to be in agreement with the experimental data by Beermann (2010) for slightly oxidizing conditions (ΔNNO; see also Fig. 8 in Webster and Botcharnikov, 2011). Based on the review of experimental data by Webster and Botcharnikov (2011), a ratio of DF-m between dacite and basalt of 50 was considered to compute the dacite partition coefficient.

To investigate the effects of silicate melt composition, the spectrum of Peteroa magmas was covered by simulating basalt and dacite degassing (Naranjo and Haller, 2002) at 1150 °C and 1050 °C, respectively. There are no data of volatile contents in melt inclusions able to constrain the pressures of the magmatic reservoirs to be used as starting conditions at Peteroa. Nevertheless, widespread presence of both plagioclase and disequilibrium textures indicates that dacite melts evolved at low pressure, whereas for basalts the increase of Al2O3 with decreasing MgO addresses to moderate pressure of differentiation. It is worth noting that the seismic activity closest to the active center of Peteroa was focused within 8 km of depth (see Sect. 3), suggesting pressures lower than 190 MPa (with 2.4 g/cm3 average density of the lithostatic column). With these constraints, the initial degassing pressures of basalt and dacite were assumed at 200 and 150 MPa, respectively. The initial N2/He, He/CO2, He/Ar* and N2/CO2 ratios of the magmatic gas phase were considered as parameters to be fit to fumarolic data, since information on the composition of the magmatic vapor at depth (e.g., fluid inclusions data) is not available.

6.3.2. Changes in the magmatic system over time

The compositions of the gas phase from decompressive degassing of basaltic and dacitic magma were computed starting from the initial conditions discussed above. The simulated data are plotted in Fig. 4a,b,c as degassing paths, and compared to the measured fumarolic compositions. It is worth noting that starting from a narrow span of initial ratios for basalt and dacite melts, the divergence of the two degassing paths is able to cover the entire compositional range of the fluid discharges, offering a new context to interpret the temporal evolution of the chemical parameters. Assuming that the initial pressure of magma degassing was 200 MPa, the composition of the 2010–2011 gases is consistent with the.
degenerating paths for basalt at 75–170 MPa, namely 3 to 6.5 km depth and CO₂ contents in the initial gas phase > 35 mol% (Fig. 4a). On the contrary, the Cl- and S-rich 2012 gases fit with the degassing pathway of a magma with a dacitic composition (Figs. 4a,b,c) at an initial pressure of 150 MPa and a CO₂ content ~ 30 mol% (Fig. 4a). This value could easily move to 45 mol% assuming an initial pressure of 200 MPa, given that these two parameters cannot be definitely constrained. The 2014–2015 gases plot in between the degassing curves of dacite and basalt, suggesting that in this period the fumaroles were fed by both magma batches degassing at 90 and 150 MPa, respectively (Fig. 4a,b). This may imply that in 2014–2015 the Peteroa magmatic system was slowly restoring the 2010–2011 conditions, as confirmed by the similar Rc/Ra and δ¹³C-CO₂ values of the 2010–2011 and the 2014–2015 fumaroles, although the latter were still showing the meteoric isotopic signature of steam that characterized the 2012 gases. It is worth noting that the basalt/dacite degassing pathway of the 2014–2015 Peteroa fluid discharges also includes the 2012 Azufre gases. This suggests that the phenomenon occurred in 2012 was mostly localized at the Peteroa summit, being able to affect Azufre only at limited extent and not modifying the chemistry of bubbling gases at the foothill of the PPAVC (Table 1).

The developed interpretative framework also allowed to model the S (and Cl) variations too. It has to be remarked that these computations are less confident than those of inert gas species, due to the poorly constrained S solubility in the melt. As shown in Fig. 5, two different initial C/S ratios were assigned to basalt and dacite in order to fit the data. The mafic melt would release an early vapor richer in C, which would be compatible with the more primitive origin of this melt. The most remarkable feature is the higher slope of the basalt degassing path with respect to that of dacite (Fig. 5). Starting from an initial N₂/He ratio of 6900 for both basalt and dacite and decreasing it to ~2200, the C/S ratio drops by 15–20 times for the dacite-released vapor, but by less than 2 times for the basalt one. Therefore, at equal N₂/He ratio, the released vapor from dacite, i.e. the 2012 gases, would be ~10 times richer in S than that from basalt feeding the 2010–2011 fluid discharges.

Taking also into account that the initial C/S ratio was lower in dacite than in basalt, a change from a basaltic to dacitic degassing magma batch is able to explain the two-orders-of-magnitude increase of acidic gases released from dacite, i.e. the 2012 gases, but by less than 2 times for the basalt one. Therefore, at equal N₂/He ratio, the released vapor from dacite, i.e. the 2012 gases, would be ~10 times richer in S than that from basalt feeding the 2010–2011 fluid discharges.

With the aim to obtain information on temperature and redox conditions of the Peteroa–Azufre magmatic-hydrothermal system and their evolution in time, gas geothermometry in the CO₂–H₂–H₂O system was carried out by considering the following pressure-independent chemical reaction:

\[
\text{CO}_2 + \text{H}_2 \leftrightarrow \text{CO} + \text{H}_2\text{O}.
\]  

The dependence on temperature of reaction (2) is given by:

\[
\log(\text{CO}_2/\text{CO}) = 2.49 - 2248/T(K) + R_H,
\]  

where R_H, i.e. log(H₂/H₂O), is the most suitable parameter describing redox potentials controlling fluids from volcanic/hydrothermal environments (Giggenbach, 1987). The grid of equilibrium temperatures ranging from 100 to 375 °C in the log(XH₂/ XH₂O) vs. log(XCO/ XCO₂) diagram (Fig. 6) was constructed by using Eq. (3). We also show equilibrium compositions at R_H values externally fixed in a vapor phase by i) the SO₂–H₂S redox pair (SO₂/H₂S: 1 and 10), typically dominating in fluids from active volcanoes and ii) the redox buffer proposed by D’Amore...
and Panichi (1980) (DP) for hydrothermal systems. All gases approached equilibrium at temperatures ≥350 °C at redox conditions controlled by the SO2–H2S buffer. The 2012 Peteroa fluid discharges had relatively low log(XH2/XH2O) values, suggesting more oxidizing conditions, in agreement with their enhanced concentrations of magmatic gases.

Further indications were gathered by considering chemical equilibria of reactions involving hydrocarbons. The Sabatier reaction between CO2 and CH4 can be expressed, as follows:

\[ \text{CO}_2 + 4 \text{H}_2 \rightarrow 4 \text{H}_2\text{O} + \text{CH}_4. \]  

In a vapor phase in equilibrium with boiling pure water, the dependence of the log(XCO2/XCH4) values on temperature and RH is given by:

\[ \log(X_{\text{CH}_4}/X_{\text{CO}_2}) = 4R_H + 5181/T + 0.14 \]  

The log (XH2/XH2O) vs. log(XCH4/XCO2) diagram (Fig. 7) shows that the CH4–CO2 pair was far from the equilibrium conditions suggested by the CO2–H2–H2O system. In fact, at the high temperatures and oxidizing redox conditions indicated by the H2/H2O and CO2/CO2 molar ratios (Fig. 6), equilibrated CH4 should be present in concentrations lower than 4 orders of magnitude with respect to those measured in the fluid discharges (Fig. 7).

The occurrence of a CH4-excess would imply CH4 addition from an “external” source. The ratios between CH4 and the sum of C2 and C3 alkanes, i.e. C2H6 and C3H8, are from 14 to 212, a range of values consistent with that of thermogenic hydrocarbons (Whiticar, 1999). This suggests that these organic species were added to the uprising magmatic material buried in the sedimentary formations surrounding the volcanic system. The relatively slow kinetic of reaction (4) would explain the limited variations of the CH4/CO2 ratio (less than 0.5 log-units) in response to the strong compositional changes occurred in 2012. On the contrary, dehydrogenation reactions of the C2 and C3 alkene–alkane pairs are considered particularly sensitive to changes of chemical–physical conditions (e.g., Seewald, 1994; Capaccioni and Mangani, 2001; Capaccioni et al., 2004; Taran and Giggenbach, 2003; Tassi et al., 2005). A generic expression for dehydrogenation of alkanes can be expressed, as follows:

\[ \text{C}_n\text{H}_{2n+2} \Leftrightarrow \text{C}_n\text{H}_n + \text{H}_2. \]  

Theoretical alkene/alkane molar ratios in the vapor phase can be computed from:

\[ \log(X_{\text{C}_2\text{H}_4}/X_{\text{C}_2\text{H}_6}) + \log(X_{\text{H}_2}/X_{\text{H}_2\text{O}}) = \log K_1 - \log P_{\text{H}_2\text{O}} \]  

and

\[ \log(X_{\text{C}_3\text{H}_6}/X_{\text{C}_3\text{H}_8}) + \log(X_{\text{H}_2}/X_{\text{H}_2\text{O}}) = \log K_2 - \log P_{\text{H}_2\text{O}} \]  

for the C2 and C3 alkene–alkane pairs, respectively. The temperature dependence of K1 and K2 is given by (Taran and Giggenbach, 2003):

\[ \log K_1 = 6.82 - 7337/T \]  

and

\[ \log K_2 = 6.32 - 5676/T(K) - 222490/T^2 \]  

where T is in K.

The log(XC2H4/XC2H6) values plotted vs. log(XH2/XH2O) (Fig. 8) confirm that the 2010–2011 and 2014–2015 gases attained chemical equilibrium in a vapor phase at high temperature (>320 °C) and redox conditions consistent with those dictated by the equimolar SO2–H2S pair, whereas the 2012 gases are shifted toward more oxidizing conditions (SO2/H2S = 10). Similar thermodynamic conditions likely controlled the C2H6–C3H8 pair (Fig. 9). Therefore, chemical reactions governing the C2 and C3 alkene–alkane had a similar behavior than those in the CO2–H2–H2O system, supporting the hypothesis that in 2012 an enhanced contribution of oxidizing (SO2-rich) fluids occurred.

7. Conclusions

The low temperature fluid discharges from the summit of PPACV are the surficial expression of a dynamic magmatic/hydrothermal system that in 2010–2015 suffered significant modifications. In February 2010 and March 2011, the chemical composition of the discharged fluids had a dominant hydrothermal signature, with relatively low concentrations of gases from magma degassing, notwithstanding the eruptive
events started in January 2010. In March 2012, just few month after the 2010–2011 eruptive activity stopped, the gases from the Peteroa summit showed a huge increase of the acidic gases and a significant decrease of the typical hydrothermal compounds (CH₄ and light hydrocarbons), apparently indicating a pulse of magmatic fluids. On the contrary, the changes in time of the R/Ra and δ¹³C-CO₂ values simulated an input of fluids from a shallow source. This apparent contradiction was tentatively explained hypothesizing a double source of magmatic fluids: (i) a basaltic magma, i.e. the deepest degassing batch that fed the gas discharges in 2010–2011; (ii) a dacitic magma, i.e. a relatively shallow batch likely affected by a significant crustal contamination, whose contribution to the fluid emissions was maximum in 2012. The occurrence of the two magma batches is supported by the basaltic and, secondarily, dacitic volcanic products recognized at PPAVC (Capaccioni et al., 2004). According to this hypothesis, in 2014–2015, i.e. when the chemical features of the fluid discharges were intermediate respect to those of the two previous periods, both the two magmatic fluid sources were active. Fluids released from the dacitic magma seem to have affected at a minor extent the gases of the Azufre volcano, located few km from the Peteroa summit. Thus, this batch likely have relatively small dimensions, as supported by the tendency shown by the 2014–2015 gases to rapidly restore the 2010–2011 fluid chemistry. It cannot be ruled out that the eruptive activity occurred in 2010–2011 at Peteroa volcano for Period 2010–2011. On the other hand, the Maule earthquake occurred in 2010 possibly had a pivotal role in triggering the 2010–2011 eruptions. In fact, large earthquakes are known to be responsible of volcanic events (e.g., Eggert and Walter, 2009), though the driving mechanisms have not clearly understood. The disturbance created by the volcanic events and the related seismic activity could have activated a silent surge triggered by the eruptive activity occurred in 2010 possibly had a pivotal role in triggering the volcanoes. Earth Planet. Sci. Lett. 222, 469–483.

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