



Behaviors of Redox-Sensitive Components in the Volcanic Plume at Masaya Volcano, Nicaragua: H₂ Oxidation and CO Preservation in Air

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Multi-disciplinary volcanic gas observations, including FTIR, Multi-GAS, and Alkali filter pack, were made at Masaya Volcano, Nicaragua, in January 2018. During the observation period, a lava lake was present, and the majority of the volcanic gases were likely emitted directly from the lava without any hydrothermal alterations. It is expected that the volcanic gas composition reflects the conditions of the magma, exhibiting a high equilibrium temperature. The fractions of the major components showed good consistency with previous studies; however, we found the fraction of the combustible components (such as H₂) were lower than expected. The R_H [log(H₂/H₂O)] value was measured to be less than -6, compared to the equilibrium R_H value calculated to be around -3 from the iron speciation. The equilibrium calculations suggest oxidation of the volcanic gases by high-temperature mixing with the air once they are emitted from the lava lake, lowering the H₂ content of the plume. In contrast to H₂, a small amount of CO, another combustible species, was detected and the derived CO₂/CO ratio of ca. 1,000 is consistent with the equilibrium magmatic value. This indicates that CO is kinetically inert compared to H₂. Our findings suggest that volcanic gases in the Masaya plume do not preserve information from when the gases were originally in equilibrium with the high-temperature surrounding magma.

Keywords: volcanic gas composition, Fourier transform infrared spectroscopy, Multi-GAS, plume chemistry, masaya volcano (Nicaragua)

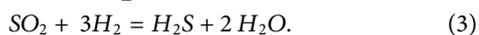
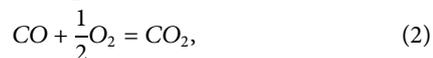
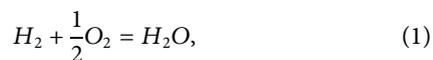
HIGHLIGHTS

- 1) The plume from the lava lake at Masaya Volcano is depleted in H₂ relative to the theoretical values from equilibrium calculations. However, CO is in good agreement.
- 2) Depletion in volcanic H₂ indicates oxidization upon mixing of the plume with air.
- 3) The chemistry of the gas plumes emitted by basaltic lava lakes may not reflect the original high temperature equilibrium at which they were emitted.

INTRODUCTION

Hydrogen (H₂) and carbon monoxide (CO) are minor components of high-temperature magmatic gases, but provide crucial clues on redox states and temperature of the magma (Giggenbach, 1987;

Moussallam et al., 2012; Oppenheimer et al., 2012). Equilibrium concentrations of these gases decrease with decreasing temperature in the gas phase after degassing from the magma via the following redox reactions with T-dependent equilibrium constants, K_1 , K_2 , and K_3 . Further details are given in **Section 4**:



If the volcanic gas is cooled slowly enough to remain in equilibrium (and without adding oxidant-rich air, i.e., closed system cooling), H₂ and CO will decrease as the equilibrium temperature is lowered. However, at lava lakes, the volcanic gases degas directly into cold ambient air, which is expected to quench the high-temperature equilibrium, preserving the concentrations of H₂ and CO. As a volcano with a lava lake, some previous studies have confirmed this at Erebus volcano in Antarctica (Table 1 in Moussallam et al., 2012). However, other volcanoes with lava lakes have suggested the possibility of oxidization of volcanic H₂, CO, and H₂S in the air for high-

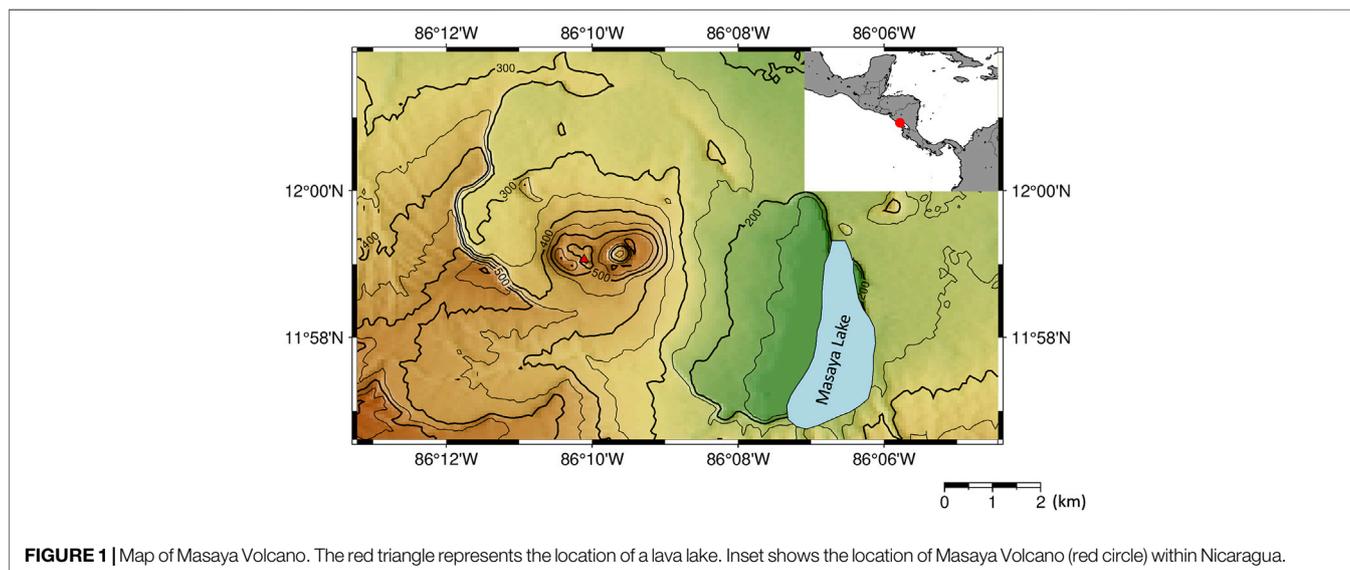
temperature volcanic gas at Erta Ale in Ethiopia and Masaya Volcano in Nicaragua (deMoor et al., 2013). Moreover, at Kilauea in Hawaii, H₂ burning has been reported (Cruikshank et al., 1973), supporting the idea that full quenching may not always occur, especially for H₂, which is more rapidly oxidized than other combustible components such as CO (Roberts et al., 2019). It is therefore important to consider if equilibrium model assumptions apply to these hot near-source plumes or not.

Masaya Volcano in Nicaragua is an open vent, basaltic volcano that has four pit craters, with recent volcanic activity centralized within the Santiago crater (**Figure 1**). In late 2015, a lava lake appeared with a very high lava flow speed (Pering et al., 2019), providing opportunities for direct observations of the active convecting magma system. Aiuppa et al. (2018) provide a detailed dataset of the volcanic gas composition from the formation of the lava lake (2014–2017). However, combustible components such as H₂ and CO have not been reported yet. In this study, we made multi-disciplinary volcanic gas measurements at Masaya Volcano to reveal the behaviors of the redox-sensitive components such as H₂ and CO in the high-temperature plume emitted from the lava lake.

TABLE 1 | Table to summarize the gas composition collected using Multi-GAS, AF pack, and FTIR. Details of all datasets can be found in **Supplementary Material S1**.

Date	Method	H ₂ O/SO ₂	CO ₂ /SO ₂	H ₂ /SO ₂	SO ₂ /HCl	HCl/HF
2018/01/09	Multi-GAS	100	3.5	*6.7 × 10 ⁻⁴	–	–
2018/01/09	AF pack	–	–	–	0.9	5.3
2018/01/10	FTIR	210	3.7	–	2.2	4.6
2018/01/11	Multi-GAS	150	3.9	*9.2 × 10 ⁻⁴	–	–
2018/01/13	Multi-GAS	120	3.8	*8.2 × 10 ⁻⁴	–	–
2018/01/13	AF pack	–	–	–	0.5	5.2
2018/01/13	FTIR	210	–	–	1.6	3.2
2018/01/15	AF pack	–	–	–	0.9	5.3
2018/01/15	FTIR	150	3.6	–	1.7	4.1

*Values are for reference because of the weak signals and the huge background errors. For details, see text.



OBSERVATION AND ANALYTICAL METHODS

FTIR

Open-Path Fourier-transform infrared spectroscopy (OP-FTIR) measures infrared-active gas species such as H₂O, CO₂, SO₂, H₂S, HF, HCl, and CO (e.g., Oppenheimer et al., 1998). Our spectrometer was a MIDAC M4410 equipped with a ZnSe beam splitter and a Stirling pump-cooled MCT detector. We used a 10 millirad, 3" Φ Newtonian telescope. The measurements were made on 10, 13, and 15 January 2018 at the south crater rim using an incandescent lamp as a source of artificial infrared radiation such that the plume flowed between the light source and the detector. The path lengths between the lamp and spectrometer were 30 m on 10 January 2018 and 40 m on 13 and 15 January 2018. An OP-FTIR measurement using a lava lake as a light source was also attempted on 12 January 2018 at a distance of a few hundred meters.

For FTIR data, the gas column amounts were calculated using simulated spectra with a forward model using spectral line parameters from the HITRAN database (Rothman et al., 2008), and finding the best fit to the field data using an optimal estimation non-linear least-squares algorithm (Burton et al., 2000). We analyzed the column amounts of SO₂ (2450–2550 cm⁻¹), H₂O (2100–2240 cm⁻¹), CO₂ (2100–2240 cm⁻¹), HF (4050–4200 cm⁻¹), and HCl (2690–2840 cm⁻¹). Analyses of CO (2070–2130 cm⁻¹) were also attempted using the data of the measurement on 12 January 2018.

Multi-GAS

Multi-GAS (Aiuppa et al., 2005; Shinohara, 2005) is a sensor-based instrument allowing us to have *in situ* measurements of gas species such as H₂O, CO₂, SO₂, H₂S, and H₂. We conducted Multi-GAS measurements on the edge of the crater rim on 9, 11, 12, and 13 January 2018. The observation points were windward relative to the FTIR. The gas sensor system consists of a non-dispersive infrared CO₂–H₂O analyzer (LI-840, LI-COR, Inc., Lincoln, United States), SO₂ and H₂S electrochemical sensors (KTS-512 and KHS-5TA, respectively, Komyo Rikagaku K. K., Kawasaki, Japan), and a H₂ semi-conductor sensor (GM12s, Sensor Tech K. K., Rittou, Japan). A SO₂ scrubber was placed in front of the H₂S sensor to reduce cross-sensitivity of the sensor (Shinohara et al., 2011). The results were recorded with a frequency of 1 Hz using a data logger (NR-1000, Keyence Co. Japan). Ambient air was pumped with a flux of 1 L/min from an inlet. The sensors were calibrated before (1 September 2017) and after (30 January 2018) the observations. The calibrations were made using gas canisters of CO₂ (ca. 400 ppm), SO₂ (ca. 50 ppm), H₂S (ca. 10 ppm), and Ar (pure gas for the zero points of the sensors). H₂O calibration was made using a dew point generator (LI610, LI-COR, INC., Lincoln, United States). The H₂ sensor was calibrated for 0.5, 1, 2, 5, 10, and 20 ppm using a gas chamber; H₂ pure gas was injected into the gas chamber using a syringe into a gas chamber to control the H₂ concentration within the gas chamber.

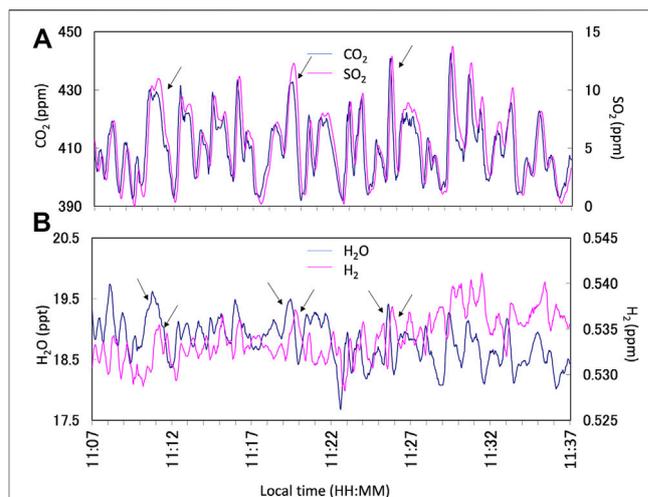


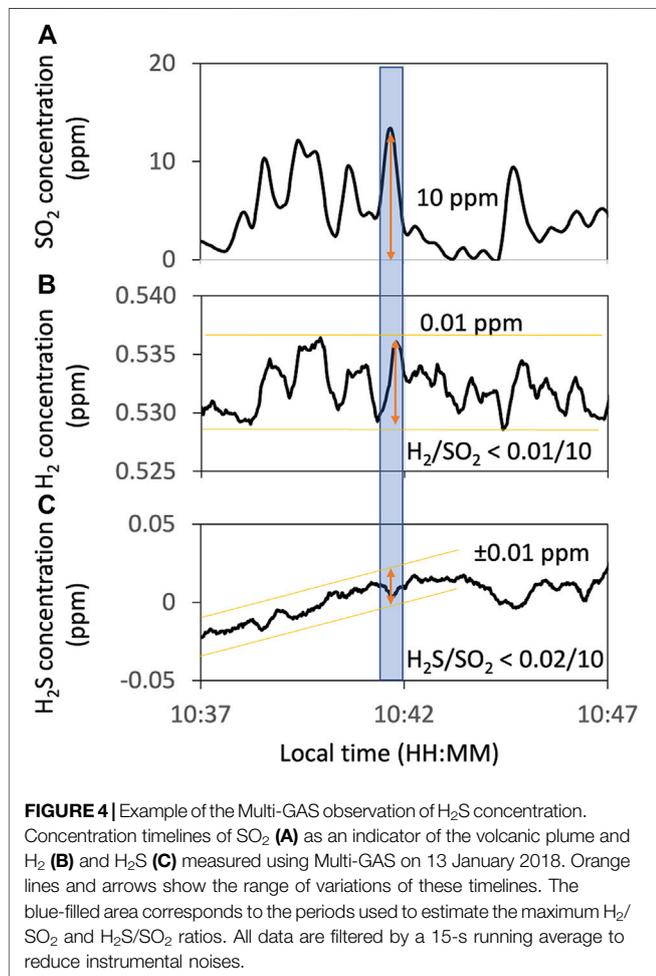
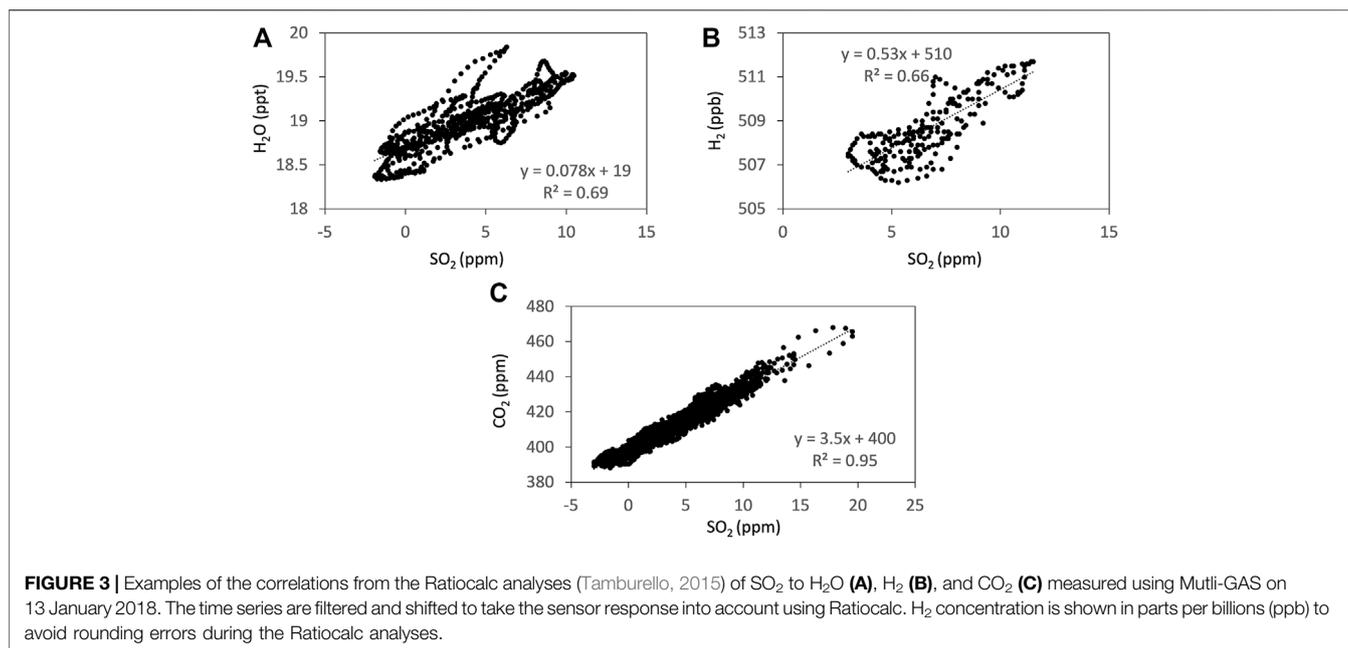
FIGURE 2 | Example of the Multi-GAS observation results on 13 January 2018. **(A)** Time series of CO₂ (blue line) and SO₂ (pink line) concentrations in parts per millions (ppm). **(B)** Time series of H₂O (blue line) and H₂ (pink line) concentrations in parts per thousands (ppt) and ppm, respectively. The arrows indicate the corresponding plume signals for the analyses. Note that the response of the H₂ signal is slow because the sensor is semi-conductor based. All data are filtered by a 15-s running average to reduce the instrumental noises. Notice that the correlation analyses were made using Ratiocalc independently.

Alkali Filter Pack

Alkali filter pack techniques (AF pack) (Shinohara and Witter, 2005; Shinohara et al., 2011) were applied to measure S, Cl, and F in the volcanic plume. The measurements were made on 9, 13, and 15 January 2018 on the edge of the crater rim alongside the Multi-GAS instrument. The filter pack includes a 0.2 μm particle filter followed by two filter holders each with two filters impregnated with 1N NaOH + 20% Glycerol. After field observations, the filters were rinsed with pure water and the solution from the filters was oxidized using hydrogen peroxide solution at GSJ, Japan. The pH was adjusted to near neutral using OnGuard-H (Thermo Fisher Scientific Inc.) before measuring the concentrations of F, Cl, and SO₄²⁻ by ion-chromatography. The first and second holders with the alkaline filters were analyzed separately. Along with the AF pack measurements, the SO₂ exposure level was monitored using a passive dosimeter tube (5D; Gastec Corporation) to ensure that the acid gases are not saturated on the filters.

RESULTS

We made parallel observations using Multi-GAS, FTIR, and AF filter at Masaya Volcano, Nicaragua from 9 to 15 January 2018. Notice that all the gas concentrations and ratios presented here are by mole. Examples of the observation results of the Multi-GAS are shown in **Figure 2**. Detection limits of the measurements depend on the observation conditions. We used signals of SO₂ as a volcanic plume indicator for Multi-GAS because ambient air contains very low concentrations of SO₂, typically 0.1–70 ppb, compared to typical dilute plume concentrations of 1–2 ppm

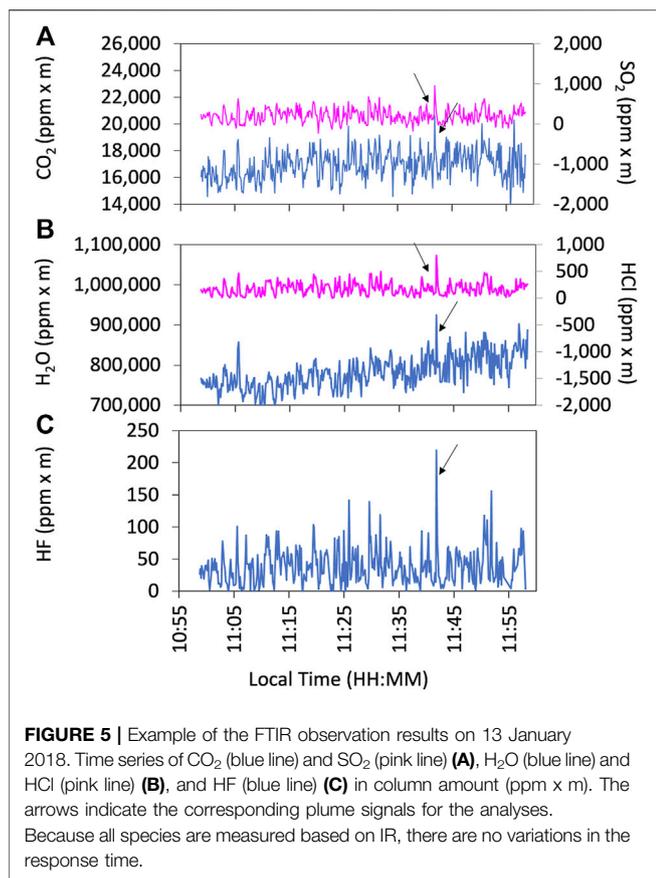


(Symonds et al., 1994). The gas ratios are derived using Ratiocalc software (Tamburello, 2015). The differences in the response times of IR-based, chemical, and semi-conductor sensors are corrected (Shinohara et al., 2011). For the correlation analysis, only data with the coefficient of determination (R^2 value) of more than 0.6 are accepted. All data analyzed with data processing information including correlation results, determination coefficients, analytical errors, and the parameters of shift and numerical filters, can be found in **Supplementary Material S1**. Examples of the correlation analyses are shown in **Figure 3**.

In Multi-GAS measurements, the concentrations of H₂S recorded are under the detection limit (**Figure 4C**). From the SO₂ signals of ca. 10 ppm and the H₂S signals of less than 0.01 ppm, we concluded that the SO₂/H₂S ratios are more than one thousand.

The H₂ signals are weak and noisy. We tried to extract the H₂ signals based on the objective criteria as follows. Using the SO₂ as an indicator of the plume, only the data where an H₂ peak appears after an SO₂ peak and the R^2 value of more than 0.6 are accepted. The correlation analysis was made using Ratiocalc software (Tamburello, 2015). The H₂/SO₂ ratio was roughly estimated to be less than ca. 10^{-3} (**Table 1**). Because this value could be artifact, we also examined if the H₂ is under the detection limit. From the SO₂ signals of ca. 10 ppm and the H₂ signals of less than 0.1 ppm (**Figure 4B**), the H₂/SO₂ ratio was estimated to be less than ca. 10^{-3} . This estimation is consistent with the H₂/SO₂ ratio derived using Ratiocalc analysis. We concluded that the H₂/SO₂ ratio is less than this value. The H₂/H₂O ratio is estimated to be less than ca. 10^{-6} using the H₂/SO₂ and H₂O/SO₂ ratios (**Table 1**).

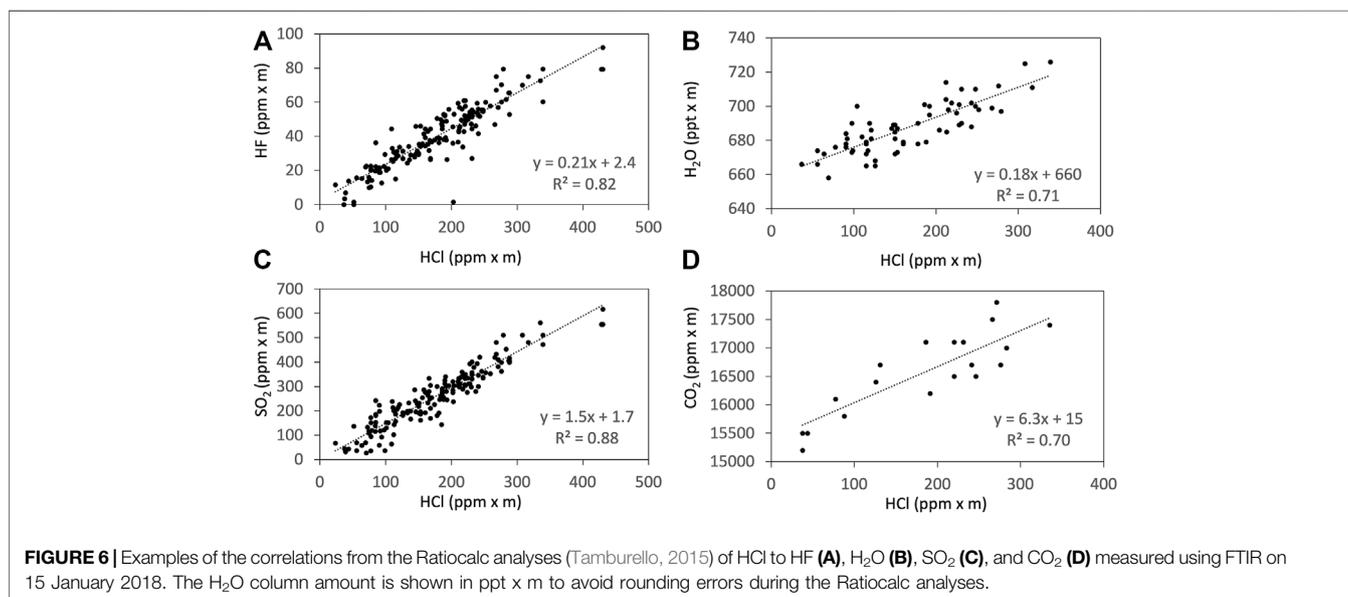
To confirm a low H₂ concentration in the plume, Multi-GAS data acquired on 19 January 2009 using the same instruments as this study were also analyzed to estimate the H₂ fraction in the

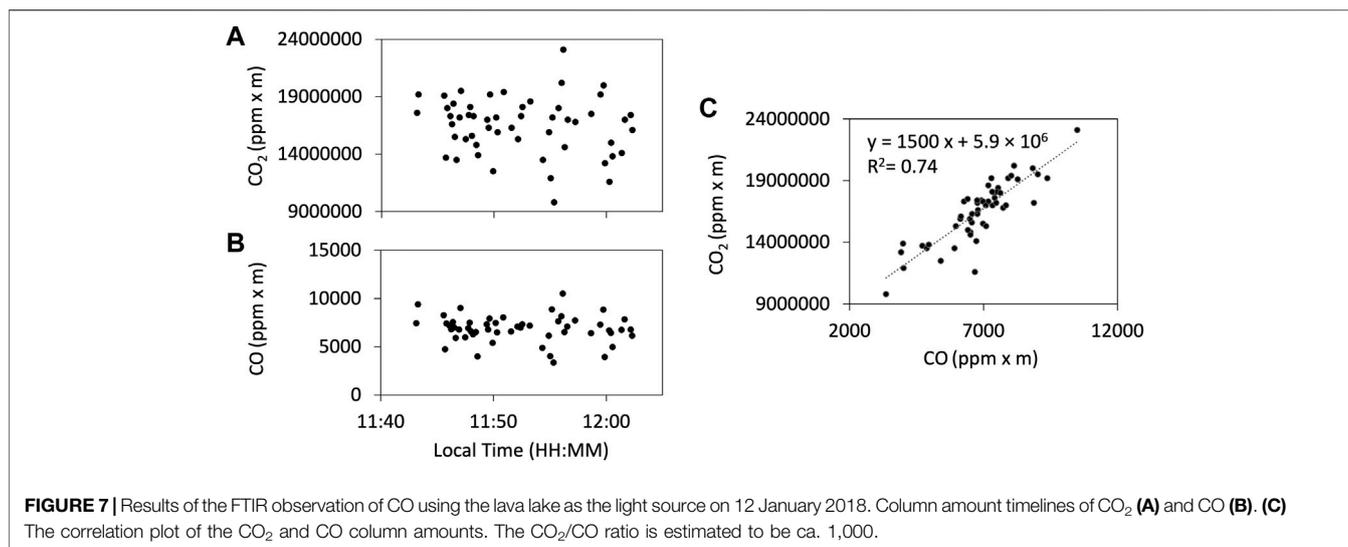


volcanic plume (**Supplementary Figure S1** in **Supplementary Material S2**). In 2009, the magma surface was within ca. 20 m of the crater floor (Martin et al., 2010). During these observations, the SO₂ sensor was broken, so, from the signal peak heights in the time series we estimated the H₂/H₂O ratios directly. Estimated

H₂/H₂O ratios of 4.9×10^{-6} were found with errors of ca. 60%, corresponding to the maximum estimation, consistent with our observation results (**Supplementary Material S1**).

Examples of the observation results of the FTIR are shown in **Figure 5**. We used HCl signals as a plume indicator for FTIR as ambient air is mostly HCl-free. The gas ratios are derived using Ratiocalc software and, as with the Multi-GAS analysis, only the data with R² values of more than 0.6 are accepted. All data analyzed with errors can be found in the **Supplementary Material S1**. Examples of correlation analyses are shown in **Figure 6**. We attempted to retrieve the column amounts of CO from the FTIR measurements, but the signals were very low as the light path was only 30–40 m. On 12 January, we made the FTIR measurements using the lava lake as the light source with a longer light path of a few hundred meters to detect volcanic CO emission. The column amounts of CO were several thousand ppm x m (**Figure 7**); the CO₂/CO ratio was calculated to be ca. 1000 using Ratiocalc software. To confirm a low CO concentration, previous FTIR data obtained in 1998 (Burton et al., 2000) were re-analyzed. As shown by comparison to Burton et al. (2000), the composition of the main gas species such as H₂O, CO₂, and SO₂ was stable. During that period, the FTIR measurements were made using incandescence from the magma pond at the crater bottom. The CO signal is very weak, with the CO₂/CO ratio roughly estimated to be 6,000 but with low correlation of the R² value of ca. 0.3 (**Supplementary Figure S2** in **Supplementary Material S2**). We concluded that the CO₂/CO ratio is as low as ca. 1,000 and more than several thousands in 2018 and 2009, respectively. This difference could be due to a change in the magmatic activity from 2009 to 2018, as discussed in **Section 4**. The CO₂/CO ratio in Masaya Volcano is significantly larger than that of 13.33 at Erebus volcano in Antarctica (Table 1 in Moussallam et al., 2012) and those of 30–180 at Kilauea in Hawaii (**Supplementary Figure**



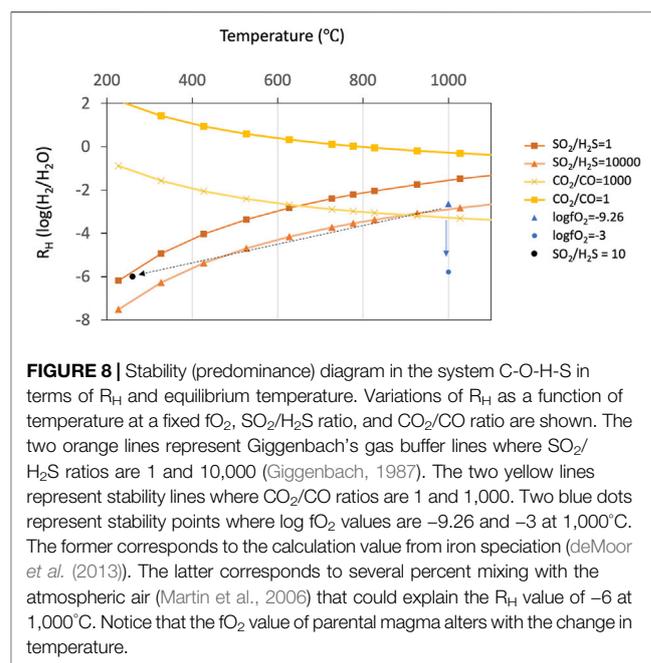


S2 in Oppenheimer et al., 2018), implying the differences in the oxidation state of the parental magmas.

The ratios of CO₂/SO₂ derived by FTIR and Multi-GAS are consistent (Table 1). The CO₂/SO₂ and H₂O/SO₂ ratios observed of ca. 4 (3.5–3.9) and ca. 150 (102–206) in this study are within the range of those reported by Aiuppa et al. (2018). The ratios of SO₂/HCl and HCl/HF observed are also comparable to those reported by Martin et al. (2010). There are disagreements between the FTIR and AF packs, as the SO₂/HCl ratios measured by the FTIR are higher (up to 4.4 times) than those of the AF packs; and the HCl/HF ratios from the FTIR are slightly lower (up to 1.7 times) than those of the AF packs. These trends are similar to the previous studies (Martin et al., 2010; Sawyer et al., 2011). The results imply that the collection of weakly acidic SO₂ may be less efficient than that of strongly acidic HCl; the same argument could be applied for weakly acidic HF and strongly acidic HCl as argued by Sawyer et al. (2011).

DISCUSSION

During the observation period at Masaya Volcano, a lava lake could be seen from the crater rim. The temperature of the lava lake is estimated to be 900–1200°C (Pering et al., 2019; INETER, 2021). The volcanic gases emitted are likely to be dominated by those degassed from the lava lake, that is, no secondary interactions with a hydrothermal system after degassing would be expected. Shallow (low-pressure) degassing is presumed (Aiuppa et al., 2018) as the CO₂/SO₂ ratios were as low as ca. 3 (Table 1). Before outgassing, the volcanic gases and magma are likely to be in equilibrium at the magmatic temperature of more than 900°C (Pering et al., 2019). After outgassing, the internal redox of the volcanic gases is thought to be quenched close to magmatic temperatures and an atmospheric pressure of 1 bar, as high-temperature volcanic gases (more than 800°C) reach equilibrium rapidly (Martin et al., 2006; Oppenheimer et al., 2018).



High H₂ concentrations are observed in high temperature magmatic gases at other volcanoes (e.g., Giggenbach, 1987; Ohba et al., 1994; Giggenbach, 1996; Henley and Fischer, 2021). The value of log(H₂/H₂O) (hereafter described as R_H) has been used as an indicator of the redox state in the gas phase (Giggenbach, 1987). The R_H values of high-temperature magmatic gases are typically from -4 to -2 (Figure 3 in Henley and Fischer, 2021). We estimate a lower R_H value at Masaya Volcano of ca. -6 using the ratios of H₂/SO₂ and H₂O/SO₂ in Table 1.

A theoretical R_H value for volcanic gas can be calculated from the oxygen fugacity (f_{O_2}). The f_{O_2} value of the magma is estimated to be of the order of magnitude of 10^{-9} at ca.

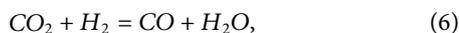
1,000°C (i.e., condition of the lava lake surface from *Pering et al.* (2019)) using the literature iron speciation measurements (Table 1 in *deMoor et al.*, 2013). The R_H value of volcanic gases with magma of this fO_2 value is calculated using the equilibrium constant of the chemical reaction 1) in the gas phase as follows (Table 1 in *Ohba et al.*, 1994):

$$\log K_1(T) = -2.076 + \frac{1576.6}{T^2} - \frac{12448}{T} - 1.6964 \times 10^{-4}T + 0.67067 \ln T \quad (4)$$

$$R_H = \frac{1}{2} \log fO_2 - \log K_1(T). \quad (5)$$

Assuming the magma temperature of 1,000 °C at an atmospheric pressure of 1 bar, the R_H value when volcanic gases and magma are in equilibrium (i.e., $\log fO_2$ of -9) is estimated to be ca. -3 (**Figure 8**). This value should correspond to the original R_H value before outgassing from the lava lake. However, the observed R_H value of ca. -6 is significantly lower.

At the same conditions described previously, the CO_2/CO ratio when the volcanic gases and magma are in equilibrium is estimated using the following reaction (Table 1 in *Ohba et al.*, 1994):



$$\log K_6(T) = 8.6753 + \frac{41163}{T^2} - \frac{2665.2}{T} + 2 \times 10^{-4} \times T - 0.92134 \ln T, \quad (7)$$

$$R_H = -\log K_6(T) - \log \frac{X_{CO_2}}{X_{CO}}, \quad (8)$$

where X_{CO_2} and X_{CO} represent the mole fractions of CO_2 and CO , respectively. When the R_H value is ca. -3 (i.e., fO_2 of 10^{-9}), at 1,000°C, the CO_2/CO ratio is estimated to be ca. 1,000 (**Figure 8**). This value is consistent with the observation in 2018, indicating that the chemical reaction (6) reaches the equilibrium

The observed R_H value of -6 at 1,000°C corresponds to the fO_2 value of more than ca. 10^{-3} , which is higher than the magmatic fO_2 value (**Figure 8**). To explain this discrepancy, we examine three possible processes: 1) additional meteoric or hydrothermal water after outgassing from the lava lake increases the H_2O content, 2) chemical reaction of the volcanic gas within the closed system (i.e., equilibrium) at low temperature, and 3) oxidization of the volcanic gas in the air to lower the H_2 content.

The process of 1) is not plausible. During the observation period a lava lake was present, so the major contribution of volcanic gases is likely to be volatiles degassed directly from the lava without any interactions with geothermal systems. Additional meteoric or non-magmatic H_2O could be emitted by low-temperature hydrothermal fumaroles along the inner crater's wall (*Aiuppa et al.*, 2018). However, the H_2O/SO_2 ratios observed are about 100 and the SO_2 emission rate from this volcano during the observation period is approximately one or two thousand tons per day (e.g., *Varnam et al.*, 2021). To lower the R_H value from -3 to -6 by adding non-magmatic H_2O , the original H_2O/SO_2

ratios equilibrated with the magma would need to be of the order magnitude of 0.1, and non-magmatic H_2O flux of more than several tens of thousands tons/day is required. Because this is not realistic, we reject this possibility.

We examined if cooling with chemical equilibrium in a closed system in the gas phase could explain this discrepancy (i.e., the possibility (b)). Within a closed system in the gas phase, the gas composition (SO_2 - H_2 - H_2S - H_2O) is thought to be controlled by the chemical reaction 3) (*Giggenbach*, 1987). The equilibrium constant and its temperature dependence are compiled by *Ohba et al.* (1994) as follows:

$$\log K_3(T) = 8.5667 - \frac{29743}{T^2} + \frac{10449}{T} + 4.7814 \times 10^{-4} \times T - 1.7784 \ln T, \quad (9)$$

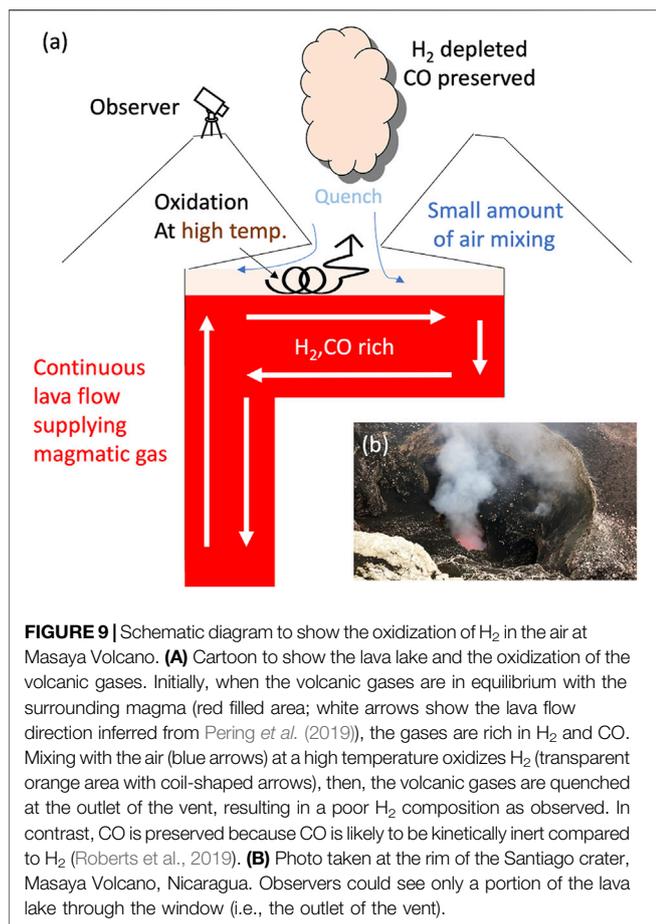
$$R_H = -\frac{1}{3} \left(\log \frac{X_{SO_2}}{X_{H_2S}} + \log fH_2O + \log K_3(T) \right), \quad (10)$$

where X_{SO_2} and X_{H_2S} represent the mole fraction of SO_2 and H_2S , respectively.

A line on R_H versus temperature plot where SO_2/H_2S ratio is a constant value is called (**Figure 8**) (*Giggenbach*, 1987). The SO_2/H_2S ratio of volcanic gases in equilibrium with the magma at 1,000 °C and fO_2 of 10^{-9} is estimated to be in the order of magnitude of 10^4 (**Figure 8**). This is consistent with the observation results that H_2S is below the detection limit (i.e., SO_2/H_2S ratio is more than one thousand) (**Figure 4**).

The simple cooling in the gas phase within the closed system (the possibility b) changes the temperature, R_H value, and SO_2/H_2S ratio simultaneously. The reaction 3) consumes 3 H_2 molecules and produces one H_2S molecule with a shift from the left-hand side to the right-hand side by cooling. If the R_H value decreases from -3 to -6 by reaction (3), H_2S is produced by one-third times the H_2 consumption. We examined the amount of H_2S production by reaction (3). Assuming that the initial R_H value is -3 (i.e., $H_2/H_2O = 10^{-3}$) and the SO_2/H_2S ratio is 10^4 at the magmatic temperature, when reaction 3) proceeds to lower the R_H value to -6 , the expected SO_2/H_2S ratio is estimated to be ca. 10 at the temperature of ca. 260°C. This value contradicts the observation results as H_2S was under the detection limit (SO_2/H_2S ratio is more than several hundred). Consequently, the simple cooling in the gas phase within the closed system cannot explain the discrepancy.

If chemical reactions occur even after mixing with the air (i.e., not quenched rapidly after outgassing), the R_H value will decrease by oxidation with atmospheric oxygen. The possibility of (c), that is, reaction 1) in the air to increase the fO_2 value to 10^{-3} (**Figure 8**) could oxidize H_2 and reduce the R_H value. Assuming an O_2 volume fraction of the ambient air of 0.21, only ca. 5 percent mixing with ambient air is needed to alter the fO_2 value to 10^{-3} . In this regard, *Martin et al.* (2006) calculated a thermodynamic equilibrium model optimized for volcanic gas chemistry and showed that the fractions of combustible components such as H_2 , CO , and H_2S decrease drastically when mixing with the air. Two clear compositional regimes divided by a compositional discontinuity were found (*Martin et al.*, 2006). They concluded that this compositional discontinuity is attributable to the amount of oxygen needed to oxidize the combustible components.



The drastic decrease in the fraction of the combustible components (H₂ and CO) occurs within the range of the mixing ratio with the air between 0 and 0.1 and at a temperature of more than 800°C. For instance, at 1,000°C, they exhibited that the R_H value of the “Arc Mean” volcanic gas (Gerlach, 2004) drastically decreases from -2 to -6 with ca. 6 percent mixing with the air (Figure 12 in Martin *et al.*, 2006). This model result is fairly consistent with our findings of an initial magmatic R_H value of -3 but an observed R_H value of -6 . However, this thermodynamic model result is inconsistent with the observation of CO not being depleted whilst H₂ is depleted; recent kinetics-based models have shown that H₂ is more readily oxidized than CO (Roberts *et al.*, 2019).

We now propose possible mechanisms that could promote the reaction of volcanic H₂ in air at Masaya Volcano and suggest directions for future research. Hydrogen has been measured using Multi-GAS at the crater rim of Erebus volcano in Antarctica, which also has a lava lake (Moussallam *et al.*, 2012). Measurements suggest that H₂ is preserved in the volcanic plume by quenching in the Antarctic cold air and it is possible that the timescale of cooling is faster than Masaya Volcano. Using this direct comparison, a simple ascent of the plume from the surface of the lava lake to the crater rim alone is not sufficient to cause oxidization attributed to mixing with the air resulting in the huge loss in H₂. To explain the H₂-depleted volcanic plume observed at Masaya

Volcano, an additional condition is necessary to oxidize the H₂ after mixing with the air.

At Masaya Volcano, the flow speed of the lava lake was estimated to be as high as 13.7–16.4 m/s (Pering *et al.*, 2019). This speed is significantly higher than other lava lake systems such as Erebus volcano (0.1 m/s) in Antarctica (Peters *et al.*, 2014). Pering *et al.* (2019) concluded that they observed only a window into lava motion processes such as the deflection of ascending magma into a surface chamber. One possible factor to cause efficient oxidization is stagnated volcanic gases at the space above the lava lake that mixes with the air driven by rapid lava flow at high temperature without quenching. A kettle-like shape of the lava lake and the upper space (i.e., the window we observe corresponds to a spout) is presumed to keep volcanic gases at a high temperature (Figure 9). Residence time of volcanic gases at the high temperature space above the lava flow for oxidation is difficult to estimate. Roberts *et al.* (2019) argued that the oxidization of volcanic gases could proceed within a time scale of seconds, but this work was for dynamics in much larger plumes. It is not clear if this time scale is applicable for the plume that we observed at Masaya Volcano. However, qualitatively, if the reaction 1) is equilibrated at a high temperature inside of the kettle-like-shaped space above the lava lake, the low observed R_H value of -6 might be explained.

If this speculation is correct, the periodicity of observed signals such as SO₂ flux could not preserve information such as bubble-burst dynamics, which would be masked by the atmospheric transportation in the kettle-shaped space above the lava lake (Figure 9). In this regard, Pering *et al.* (2019) reported periodicity of 200–300 s oscillations in SO₂ flux which could also not be seen in the volume of the gas in bubble bursts. They similarly concluded that the periodicity may not be attributed to the volcanic/magmatic process, but to atmospheric mechanisms such as atmospheric transport and turbulence.

These observations imply that volcanic gases are oxidized in the kettle-shaped space above the lava lake, depleting them in H₂ by mixing with the air at a high temperature (Figure 9). The observed gas composition is likely to be superimposed by oxidation in air and would not preserve the magmatic information. On the other hand, the high H₂ concentration at Erebus volcano in Antarctica (Moussallam *et al.*, 2012) might be attributable to the quenching of the volcanic gas immediately after outgassing as there are no spaces above the lava lake to keep the volcanic gas at a high temperature and/or due to rapid cooling in the cold Antarctic atmosphere.

In contrast, the CO₂/CO ratio of ca. 1,000 in 2018 corresponds to the equilibrium temperature of 1,000°C and magmatic fO_2 of 10^{-9} (Oppenheimer *et al.*, 2019), indicating that CO is not lost by the oxidization in the air. This result is consistent with the simulation results from Roberts *et al.* (2019), showing a relatively inert characteristic of CO comparing to H₂. The difference in the CO₂/CO ratio between 1998 and 2018 could simply be explained by a cooler, less active surface lava lake in 1998, causing equilibrium at a slightly lower temperature (900°C corresponding to the CO₂/CO ratio of 6,000 rather than 1,000°C). Considering the more active degassing in 2018 (Aiuppa *et al.*, 2018) compared to 1998, we consider this a likely explanation of the difference.

At volcanoes without lava lakes (e.g., Giggenbach, 1987; Aiuppa et al., 2011; Shinohara et al., 2018; Kazahaya et al., 2019; Ohba et al., 1994; Henley and Fischer, 2021) H₂ and CO are detected, and the chemical equilibrium has been discussed to get insights into undermined magmatic/hydrothermal processes. It is also important to elucidate if the heat supply from the lava lake to volcanic gases is required for the oxidization after outgassing.

The high-speed lava flow (13.7–16.4 m/s at Masaya Volcano; Pering et al. (2019)) may be the key for the effective oxidization of the volcanic gas in the air. Similar atmospheric oxidations could take place at other volcanoes such as Ambrym, Vanuatu, which have a lava lake with a lava flow speed of 5 m/s (Radebaugh et al., 2016) or volcanoes where the H₂ of the volcanic plume is under the detection limit such as Villarica, Chile (Sawyer et al., 2011; Moussallam et al., 2016).

In this study, we argue that the possibility of the oxidization of the volcanic gases attributed to mixing with the air at a high temperature by a simple predominance examination in the system C-O-H-S (Figure 8). However, detailed conditions such as the temperature, mixing ratio of the air, and residence time required to oxidize the volcanic gases are difficult to quantify. One future direction could be given by a plume chemistry model to handle the reaction rates controlling the composition of the volcanic gases in the air (Roberts et al., 2019) combined with a physical model of atmospheric turbulence and heat supply for ash-free plumes. The details of the oxidization processes may need to be examined extensively, not only using volcanic plumes with detectable H₂, but also those depleted in H₂ such as our study site, Masaya Volcano.

CONCLUDING REMARKS

We conducted volcanic gas observations at Masaya Volcano, Nicaragua, in January 2018 with a lava lake present. H₂S was under the detection limit and the observed H₂/H₂O was surprisingly low, with an R_H value of less than -6. This low R_H value is significantly lower than the expected R_H value of -3 calculated from petrological insights (temperature and fO₂). To explain this discrepancy, we proposed that the oxidization in air at a high temperature would play a role controlling the H₂ fraction. These results suggest that H₂ is oxidized by several percent mixing with the air to increase the fO₂ value from the magmatic value (10⁻⁹) to the order of magnitude of 10⁻³.

One key feature of the lava lake in Masaya Volcano is a very rapid lava flow with speeds of 13.7–16.4 m/s (Pering et al., 2019). It is possible that this rapid lava flow encourages effective mixing with the air, oxidizing the volcanic gas. A kettle-like shape around the vent is considered so that the volcanic gases can be stagnated above the lava lake with the air and oxidize at a high temperature.

Martin et al. (2006) and Roberts et al. (2019) proposed the plume chemistry model to discuss the oxidization of volcanic components such as H₂, CO, and H₂S. At Masaya Volcano, the possibility of combustion of H₂ has been argued by deMoor et al. (2013). Our results support their ideas. The observed volcanic gas composition, depleted in H₂, is likely the result of masking by atmospheric oxidization processes, so the gas composition observed does not reflect the original magmatic H₂.

On the other hand, the CO₂/CO ratio of ca. 1,000 observed in 2018 is consistent with the magmatic value with an equilibrium temperature of 1000°C. This implies that CO is not likely to be lost by the oxidization in the air. This hypothesis is consistent with the insight from the simulation results of Roberts et al. (2019) that pointed out that CO is kinetically less reactive comparing to H₂.

Our results show that care must be taken to consider the effect of oxidization in the air, especially when quantifying the composition of high-temperature volcanic gases, when measuring the resulting mixture of volcanic gases and ambient air (e.g., Multi-GAS and FTIR). Lava lakes might traditionally be thought of as unlikely to be affected by secondary alterations such as hydrothermal processes. However, we show that even gas compositions emitted from lava lakes could be superimposed by atmospheric oxidation. Such gases therefore do not necessarily preserve magmatic information. At Masaya Volcano, the results from physical observations (i.e., the speed of lava flow and structure of the upper space above the lava lake) complement the puzzling volcanic gas composition observed to elucidate the processes of oxidization. Multi-disciplinary assessments and model calculations are crucial in solving these puzzles, especially in the interpretation of the complex datasets.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

RK drafted the manuscript. RK, MV, BE, and MI collected the data in the field and analyzed them. MB and HS analyzed the volcanic gas data. All authors read and approved the final manuscript.

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: <https://www.frontiersin.org/articles/10.3389/feart.2022.867562/full#supplementary-material>

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