

Magmatic signature in acid rain at Masaya volcano, Nicaragua: Inferences on element volatility during lava lake degassing

Marcello Liotta^{a,*}, María Martínez Cruz^b, Arnoldo Ferrufino^c, Julian Rüdiger^d,
Alexandra Gutmann^e, Kathia V. Rojas Cerda^f, Nicole Bobrowski^g, J. Maarten de Moor^b

^a Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo, Palermo, Italy

^b Observatorio Vulcanológico y Sismológico de, Costa Rica Universidad Nacional (OVSI-CORI-UNA)

^c Instituto Nicaraguense de Estudios Territoriales, Dirección de Geofísica INETER, Nicaragua

^d Environmental Chemistry, Technical University of Berlin, Germany

^e Institute of Inorganic and Analytical Chemistry, Johannes Gutenberg-University Mainz, Mainz, Germany

^f Centro de Investigación en Recursos Acuáticos de Nicaragua CIRA UNAN-Managua, Nicaragua

^g Institute for Environmental Physics, University of Heidelberg, Heidelberg, Germany

ARTICLE INFO

Editor: Dr. Hailiang Dong

Keywords:

Masaya volcano
Volcanogenic elements
Single rainfall events
Volatility
REEs

ABSTRACT

Major, minor and trace element concentrations of single rainfall events were investigated at Masaya volcano (Nicaragua) in order to determine the relative contributions of volcanogenic elements. Most of the samples were collected in the summit area of the volcano around the Santiago crater, and two samples, representative of the local background, were collected at a 4.3 km upwind site. Samples from the summit are very acidic with pH down to 2.14 and contain large amounts of volcanogenic elements that can be clearly distinguished from the local background. These elements are released into the atmosphere from the continuously degassing lava lake of the Santiago crater, Masaya volcano. The emissions result in a volcanic plume that includes solid particles, acidic droplets, and gaseous species. The plume-rain interaction imprints the chemical signature of the volcanic emissions in falling raindrops. The most acidic gases (e.g. HCl and HI) readily dissolve in water, and so their ratio in rain samples reflects that of the volcanic plume. The transport of HF is mediated by the large amount of silicate particles generated at the lava–air interface. SO₂ is only partially converted into H₂SO₄ that dissolves in water. The refractory elements dissolved in rain samples derive from the dissolution of silicate particles, and most of them (Al, Mg, Ca, Fe, Be, Ti, Mn, and Sr) are present at exactly the same molar ratios as in the rocks as well as rare earth elements (REEs). By contrast, Li, Na, K, Cr, Ni, Cu, Zn, Rb, Cd, Sb, Te, Cs, Tl, Pb, and Bi are enriched relative to the whole-rock composition, suggesting that they are volatilized during magma degassing. After correcting for the dissolution of silicate particles, we can define the relative volatility of these elements. The comparison with other volcanoes on the Pb emissions highlights the effect of oxygen fugacity in determining its volatility.

1. Introduction

Volcanic plumes carry large amount of gases and particles towards the atmosphere (Mather, 2008; Mather et al., 2012). The most volatile elements leave the magma body as gaseous species (H₂O, CO₂, SO₂, HCl, HBr, HI) while the most refractory (Si, Al, Mg, Sr etc.) are emitted as constituents of solid particles. Some elements behave as semi-volatile (e.g. Na, K, Rb, Cd, Pb, Cu) and are emitted as both gaseous phases (mainly as chlorides) and solid particles (Mather, 2015 and references therein). Understanding the processes occurring during magma degassing and

during the interaction with the surrounding atmosphere is a key to properly evaluating the mobility of volcanogenic elements and their effect on the environment (Gauthier and Le Cloarec, 1998; Calabrese et al., 2011; Mather et al., 2003; Mather et al., 2012; Cuoco et al., 2013; Liotta et al., 2017). Volcanoes hosting lava lakes are perfect natural sites where scientists can conduct experiments to improve the understanding of geochemical processes taking place at the lava-atmosphere interface and in the ageing plume. The emitted gases and particles also influence the chemical composition of precipitation. Interaction processes between volcanic plumes and falling raindrops leave clear signatures in

* Corresponding author.

E-mail address: marcello.liotta@ingv.it (M. Liotta).

<https://doi.org/10.1016/j.chemgeo.2021.120562>

Received 31 May 2021; Received in revised form 1 October 2021; Accepted 2 October 2021

Available online 5 October 2021

0009-2541/© 2021 The Authors.

Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

(<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

water and provide the opportunity to retrieve useful information on volcanic emissions as well as to evaluate their environmental impact. At Nyiragongo and Nyamulagira volcanoes (Democratic Republic of Congo), where the persistent plumes strongly affect the environment and human health (Balagizi et al., 2017), the chemical composition of rain provided useful information on mobility of plume-derived volcanogenic elements and on their relative volatility (Liotta et al., 2017). At Erta Ale north pit crater, Zelenski et al. (2013) observed that in fumaroles chalcophile elements (Cd, Cu, Zn, Se, Te, As) were mainly transported in the gaseous form while alkali metals were partially emitted as liquid micron-size sulfate droplets and alkali earths, aluminum, and REE had a high affinity to silicate aerosol in the form of basaltic microspheres.

Masaya volcano is particularly interesting from a petrological point of view. Basalts from Masaya exhibit an unusually homogeneous composition over time (Walker et al., 1993), and their compositions mirror the olivine-hosted melt inclusions compositions while plagioclase-hosted melt inclusions have generally higher K₂O contents (Zurek et al., 2019). The variability of the chemical composition of whole rocks falls within a fairly narrow range of the basaltic tholeiitic field (Fig. 1b). At Masaya, the magma generation processes include the contribution of a depleted mantle source and subducted sediment clearly testified by ¹⁰Be/⁹Be (Carr et al., 2007). Based on volatile content in melt inclusions and groundmass glass of rock samples, Zurek et al. (2019) found that sulfur is extensively degassed from magma during the eruptions whereas more than 50% of chlorine remains dissolved in the melt. This is common also at other basaltic volcanoes such as Mt. Etna (Spilliaert et al., 2006a, 2006b). During magma differentiation and crystallization, the elements behave differently depending on their chemical properties. While elements such as Si, Al, Fe, Na, Mg, and Ca easily enter cation sites in minerals, incompatible elements have very low partition coefficients with respect to the most common minerals. They include large-ion lithophile elements, rare-earth elements and high-field-strength elements. Incompatible elements tend to stay in the liquid phase and are hence available to be partitioned into the vapor phase during eruption depending on their volatility.

A significant amount of scientific literature describes the chemical composition of the volcanic plume and its impact on the environment at Masaya volcano. Delmelle et al. (2002) found that the volcanic emissions from Masaya influenced air quality across a 1250 km² area downwind and can dramatically affect acid deposition downwind and in turn cause extreme acid loading of the local ecosystems (Delmelle et al., 2001). Vallelonga and Mather (2003) reported Pb concentrations and isotopic compositions measured in plume aerosol and Pele's hair samples collected from Masaya volcano. The authors found that a large fraction of the total emitted Pb was present in the fine aerosol (being

96% in the dry daytime plume to 61% in the condensed night-time plume). They computed Pb fluxes from Masaya to be 1.0 ton yr⁻¹ with a mean plume Pb/S_(gas) ratio of 1.3×10^{-5} (weight ratio that corresponds to 2×10^{-6} M ratio). Moune et al. (2007, 2010) focused on the chemical composition of solid particles (Pele's hairs and tears, spherical silicate particles and aerosol) and observed a siliceous enrichment in edges of tears and hairs with respect to the inner parts. In order to determine trace elements in the aerosol phase, Moune et al. (2010) sampled the volcanic plume using a single-stage filter pack and found that the most abundant trace elements in the aerosol phase are Cu, Zn, Ba, Tl, Rb, Pb, Cd, Te, Sr, and Bi. Unfortunately, they did not determine major elements concentration in filter sample thus were unable to clearly distinguish the trace element abundances coming from the dissolution of silicate particles. Based on the REE concentrations in the aerosols phase normalized to lava composition, they suggested a possible degassing of light rare earth elements (REEs) as chlorides. More recently, Martin et al. (2012) investigated the emission of trace elements from Masaya volcano through measurement of high-resolution trace element size distributions using cascade impactors. They observed that volatile elements such as As, Cd, Tl, Cu, Pb, and Zn exist in the plume as fine sulfate, coarse sulfate, and coarse chloride. They proposed that trace elements released from the magma as chlorides react rapidly with H₂SO₄ in the plume to form sulfates. On the other hand, non-volatile elements exist primarily as spherical silicate particles in the 1–10 μm range emitted by magma ejection. In addition, Martin et al. (2012) also argued that primarily volatile degassing does not emit REEs.

Although that rain events represent a natural sampling source of most of the plume components (e.g. Calabrese et al., 2011; Liotta et al., 2017), only Johnson and Parnell (1986) previously investigated the chemical composition of precipitation at Masaya, but they focused solely on a limited number of elements and on the neutralization of acid rain. The aim of the present study is to characterize and understand the processes affecting the composition of acid rain at Masaya volcano. Since degassing represents an important source of volcanogenic elements that affect the surroundings of the volcanic systems, the understanding of the processes governing the rain-plume interaction is fundamental for constraining the environmental impact of volcanic emissions. Based on the comparison with available data of rocks and silicate particles at Masaya, we define, for the first time to our knowledge, a volatility scale of the elements.

2. Sampling and analytical methods

The chemical composition of single rainfall events was investigated at Masaya volcano (Nicaragua) (Fig. 1) with the aim of determining the contributions of plume-derived elements. During the campaigns in July

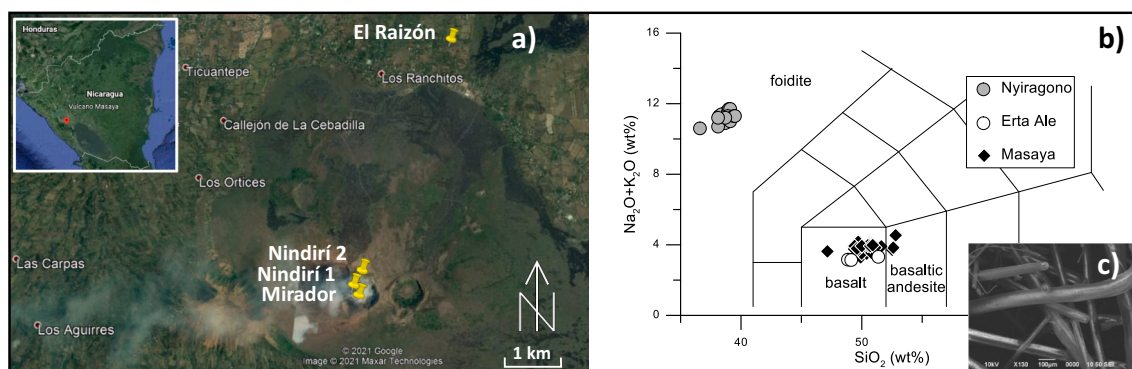


Fig. 1. a) Satellite view of Nicaragua (in the inset) and Masaya volcano. Sampling sites (yellow pins) are labeled as in Table A1 on a base map from Google Maps (2021). b) Total Alkali Silica (TAS) diagram showing the limited compositional range of basaltic rocks for Masaya over the last 6000 years. Data are from Walker et al. (1993), Carr et al. (2014) and Zurek et al. (2019); the rock composition of recent lava flows at Nyiragongo volcano (Chakrabarti et al., 2009) and Erta Ale volcano (Field et al., 2012) are also shown for comparison. c) SEM image of Pele's hairs collected at Masaya (photo courtesy of M.M. Cruz). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

and September 2016 we collected 12 rain samples at three sites around the Masaya Santiago crater (Nindirí 1, Nindirí 2 and Mirador) and 2 rain samples from a site not affected by the volcanic plume (El Raizón, see Fig. 1) (sampling dates are given in the Appendix Table A1). Solid particles are highly abundant in the summit area, especially in the form of Pele's hair and tears (Moune et al., 2007). The rain gauges were bulk collectors that remained open with a low density polyethylene mesh (5×5 cm) to prevent the entrance of debris such as insects and leaves, throughout the sampling period (2 to 10 h), and thus received both wet and dry deposition from the atmosphere. The use of bulk collectors to sample rain can result in further modifications in the chemistry of the collected rainwater due to the accumulation of particulate matter and/or direct chemical exchange with gas if the sampling site is in direct contact with plumes. In order to minimize this effect, we filtered (using Sartorius cellulose acetate membrane filters with a pore size of $0.22 \mu\text{m}$) the samples immediately after collection in the field, which was usually only a few hours after the rain event. We also sampled the volcanic plume emitted from the Santiago crater by using active alkaline traps (Wittmer et al., 2014; Rüdiger et al., 2021) in order to compare the chemical composition of gas emissions with that of the rainwater.

Rain samples were then analyzed at the Istituto Nazionale di Geofisica e Vulcanologia (Sezione di Palermo). The pH measurements were performed using a Mettler Toledo electrode model DGI 115-SC connected to a compact titrator model G20. We determined major inorganic anions (F^- , Cl^- , NO_3^- , SO_4^{2-}) and cations (Na^+ , NH_4^+ , K^+ , Mg^{++} , Ca^{++}) using an ion chromatography system (ICS-1100, Dionex) in suppressed mode and equipped with an anion column (AS14A) and a pre-column (AG14A) that works under continuous flow of the carbonate-bicarbonate eluent, and a cation column (CS12A) and pre-column (CG12A) that works under continuous flow of methanesulfonic acid with eluent regeneration; precision and accuracy of the method are described

in Prano and Liotta (2017). Major and trace elements were also analyzed by inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500-ce) and inductively coupled plasma optical emission spectroscopy (ICP-OES, Jobin Yvon Ultima2 for Si, Al, Fe, Mn). The analytical accuracy of trace-element determinations was checked by the analysis of four Certified Reference Materials (TM Rain 04, SLRS5, SPSSW1, SPSSW2) specific for the analysis of trace elements in fresh rain water. The deviation between certified and measured values is about 5–7% for the majority of elements (Table A1).

3. Results

The abundances of the analyzed elements are plotted in Fig. 2 and provided as Appendix (Table A1). Most of the rain samples were very acidic with pH ranging between 2 and 3 for the near crater samples and containing large amount of F and Cl. The samples collected at El Raizón represent the local background. Their chemical composition is very similar to the average composition of samples (not plume-affected) collected by Johnson and Parnell (1986) and to the volume-weighted average composition of rain samples collected between 1979 and 1981 at Turrialba canton 25 Km south-east and upwind of Turrialba volcano (Costa Rica) (Hendry et al., 1984). With respect to the dataset of Johnson and Parnell (1986), Na Mg, and Cl are more abundant in El Raizón samples, while with respect to the dataset of Hendry et al. (1984) Ca and NO_3^- are more abundant in El Raizón samples. In samples collected in the summit area of Masaya most of the elements are higher with respect to the local background. The elements with the highest concentrations (>0.01 mmol/L) are H, F, Cl, S (as SO_4^{2-}), Si, Al, and Fe. Meanwhile, NO_3^- , B, Zn, and Sn show similar values in the local background and in samples from the summit. F, Be, Ti, Cu, Mo, Te, Cs, Tl, Bi, U, Y, Hf, and REE were not detected in the local background with their

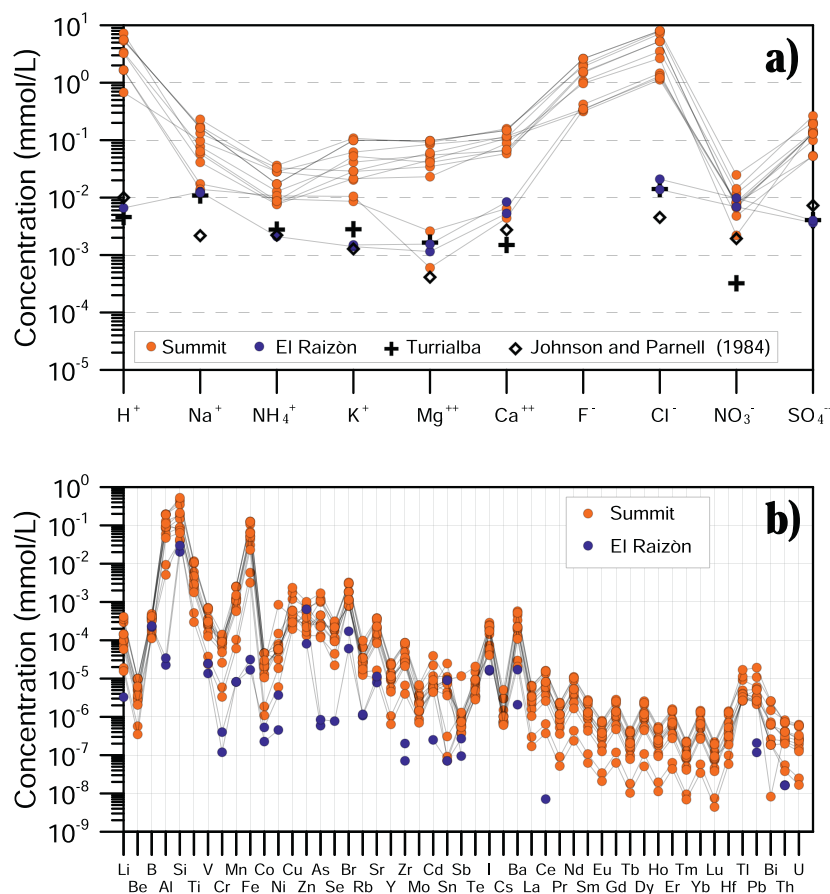


Fig. 2. Concentrations of major (a), minor and trace elements (b) in the summit area (orange dots) and at El Raizón site (blue dots). Average composition of rain samples non affected by the plume from Johnson and Parnell (1986) and volume weighted average concentrations from Turrialba canton (Costa Rica) (Hendry et al., 1984) are also plotted (black diamonds and crosses respectively) for comparison. a) gained by IC-analysis and pH electrode, b) with ICP-MS and ICP-OES. In b) elements are arranged according to their atomic number. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentrations being below detection limits. Results on the plume composition are given and discussed in Rüdiger et al. (2021).

4. Discussion

4.1. Volatile plume-derived elements in precipitation

Results clearly indicate that the chemical composition of samples from the summit crater is strongly affected by the volcanic plume. The high content of H^+ , F^- , Cl^- , and SO_4^{2-} is the result of the dissolution of acidic gases in raindrops and/or leaching of silicate particles as already observed at other volcanoes such as Nyiragongo (Liotta et al., 2017), Mt. Etna (Calabrese et al., 2011), Stromboli (Liotta et al., 2006; Bagnato et al., 2011). In order to evaluate the dominant processes, we compared the volatile elements' ratios in precipitation with those measured in the volcanic plume (Fig. 3).

In plume-affected rainwater samples, the I/Cl molar ratios overlap those measured in the volcanic plume while Br/Cl only partially overlap. This depends on the fact that volatile elements (except for sulfur) are dominantly emitted as acidic gases HCl, HF, HI, and HBr and promptly interact with liquid/vapor water. Still, their dissolution is mainly determined by their acid dissociation constants (being $pK_a = 7, 3.2, -9$ to $-9.5, -8$ to -9 respectively at $25\text{ }^\circ\text{C}$; Perrin, 1969), and on the adsorption capacity of volcanic ash and particles, this latter is in particular seen for HF. The dissolution and dissociation of the most-acidic gases (HCl, HI, and HBr) directly leave their mark in raindrops thus producing very similar ratios in rain samples and plume (Fig. 3). However, we can appreciate that Br/Cl ratios are lower most of the time than those measured in the volcanic plume. This reflects the fast bromine speciation to form less soluble Br species (e.g.: Br_2 , Rüdiger et al., 2021).

Interestingly, the F/Cl ratios of the plume-affected rain samples are systematically higher than those measured in the plume despite the fact that HF is a weak acid. This is probably due to the different mobility mechanisms of HF. Even if HF is a weak acid, leachates of volcanic ash indicate that F^- is easily adsorbed by ash, which results in its enrichment in leaching solutions (Delmelle et al., 2007; Bagnato et al., 2011). As already observed at Nyiragongo (Liotta et al., 2017), solid particles, in the form of Pele's hair and tears, can act as HF adsorption nuclei. Similarly, Masaya's Pele's hair and tears indeed contain high amounts of F, as observed by SEM-EDS (Martínez, pers. comm.). Wolff-Boenisch et al. (2004) demonstrated that the presence of aqueous fluoride in acid solutions increases significantly natural glass dissolution rates. Consequently, the interaction of HF with the silicate particles favors the dissolution of glass matrix. The SO_4^{2-}/Cl^- ratios in plume-affected samples is significantly lower than those measured in the plume (Fig. 3d). The oxidation of SO_2 to form H_2SO_4 and SO_4^{2-} is not immediate and occurs through the photochemical reactions involving hydroxyl radical (OH) and Criegee intermediates (Bekki, 1995; Welz et al., 2012; Rose et al., 2020 and references therein). In addition, SO_2 can be taken up by cloud droplets and aerosol and undergo aqueous phase oxidation. In the aqueous phase, oxidation mainly occurs by reaction with H_2O_2 or O_3 , with the O_3 reaction becoming greater than typical gas phase reaction rates at pH higher than approximately 4 (Seinfeld and Pandis, 2006). Thus, the kinetic for SO_2 to be oxidized to H_2SO_4 and dissociated in water plays an important role. Direct measurements in volcanic plumes are scarce, however at Erta Ale volcano Zelenski et al. (2013) found that the molar ratio of H_2SO_4/SO_2 in the plume was very low (i.e. 0.0082 ± 0.0025), thus confirming the low reaction rate. Consequently, the SO_4^{2-}/Cl^- ratio in rain is lower than that of the plume due to only partial oxidation of SO_2 .

4.2. Refractory and semi-volatile elements in precipitation

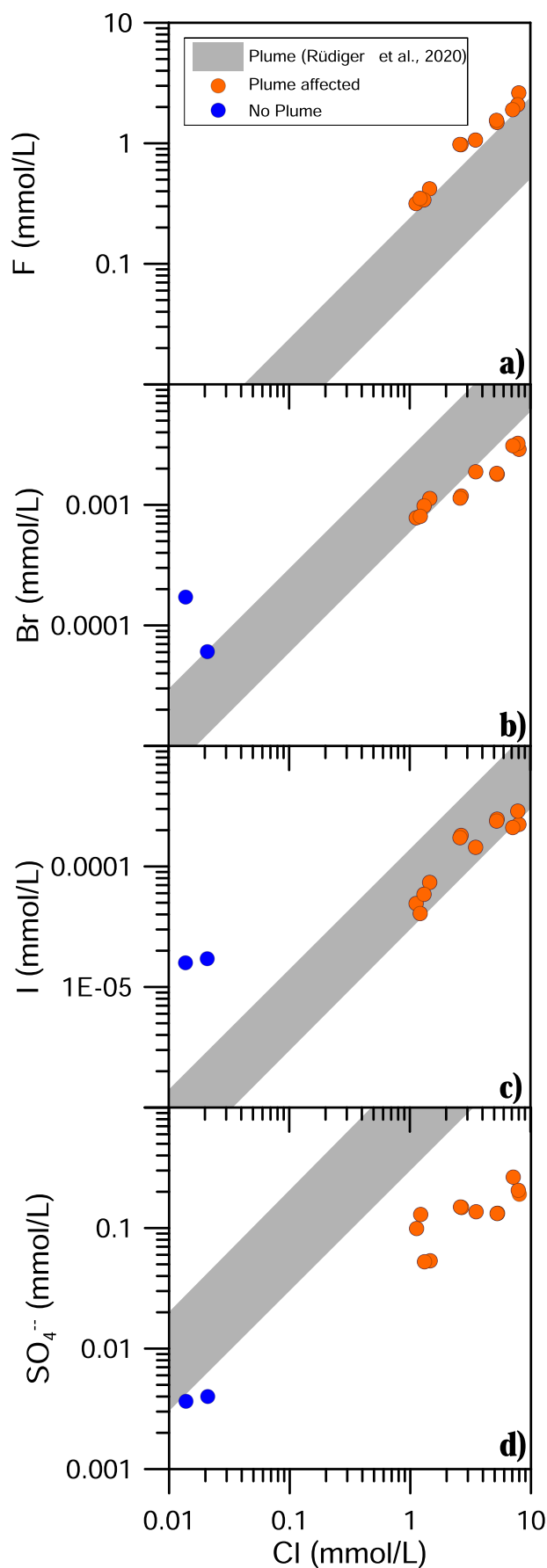
The high content of refractory lithophile elements such as Si, Al, and Fe is the result of acidic leaching of silicate particles (Pele's hairs and

tears, spherical particles). The most effective method to evaluate if the chemical composition of acidic rain samples reflects isochemical dissolution of silicate particles of the volcanic plume is to compute the enrichment factor (EF) with respect to the rock composition, normalized to a refractory element that is abundant in the rock and shows a high mobility in acidic environments according to:

$$EF = \frac{\left(\frac{X_{rain}}{Y_{rain}}\right)}{\left(\frac{X_{rock}}{Y_{rock}}\right)} \quad (1)$$

where X is the concentration of the element of interest, Y the concentration of the reference element chosen for normalization, and subscripts indicate the sample type. The most abundant element is silicon but findings from literature clearly point out that, under acidic leaching, silicon has a low mobility and tends to form a coating on silicate particles and rocks (Moune et al., 2007; Chemtob and Rossman, 2014). Under these conditions, the best choice is to normalize with respect to Al or Fe. We prefer to normalize with respect to Al (Fig. 3) because Fe can exist as both Fe^{2+} and Fe^{3+} and its mobility can change from location to location. Since the chemical composition of rocks does not show wide variations over time (Walker et al., 1993; Zurek et al., 2019), in order to compute the enrichment factors we have chosen the most recent and complete rock analysis from Moune et al. (2010) and Carr et al. (2014). When the computed EFs are close to 1, the element exhibits the same mobility of the element used for normalization. Conversely, when the EFs are higher or lower than 1 they indicate enrichment or depletion, respectively with respect to isochemical dissolution of silicate particles. Since the processes responsible for the chemical composition of rain samples include the interaction of rainwater with both gaseous and solid particles, the enrichment of an element in the rain samples is a proxy for its volatility. Indeed, while depletion of an element could depend on its low mobility (this is the case of Si), the enrichment necessary implies a further source than silicate particles. In volcanic plumes the other possible source are gases and aerosol forming by condensation of volcanic gases, transformations of existing particles and low temperature reactions (Mather et al., 2004). Regardless of the way in which the volcanogenic elements travel through the plume, their abundances reflect two main processes: lava fragmentation (producing silicate particles) and volatilization (producing non-silicate particles). Consequently, the degree of enrichment of the elements with respect to the rock reflects their volatility.

All the alkali metals (Li, Na, K, Rb, Cs) are moderately enriched in rain samples (Fig. 4). Volatilization of alkalis from basalts has been known since the 1970s (De Maria et al., 1971; Storey, 1973), although studied under different conditions (e.g. vacuum conditions). Among the transition metals, Cr, Ni, Cu, and Zn are also enriched with respect to the rock composition. In the same range of EF we find the heavy metal Pb and the metalloid Sb. The most enriched elements are Cd (heavy metal), Te (metalloid), Tl (metal), Bi (metal). These elements have already been observed to be highly volatile by Martin et al. (2012) based on the chemical composition of size resolved particulate samples at Masaya, and by Liotta et al. (2017) based on the chemical composition of plume-affected rain samples at Nyiragongo. All the REEs have EF close to 1, indicating that they come from the dissolution of silicate particles and behave as refractory elements. The EFs thus provide a first evaluation of different volatility of the elements but are imprecise when considering that different relative contributions of solid and gaseous phases enable accurate computations. In fact, during their fall, raindrops interact with different plume components: gaseous, soluble-salt, and silicate particles. In addition, raindrops already contain some dissolved elements before interacting with the plume. The relative contribution of the local background can be easily recognized by taking into account the chemical composition of the samples from the upwind site El Raizón. With few exceptions (NO_3^- , B, Zn, Sn) the relative contribution of the local



(caption on next column)

Fig. 3. Cl versus Br, F, I, and SO_4^{2-} in precipitation. Blue dots indicate upwind samples (El Raizón), orange dots indicate samples from the summit of Masaya. Gray bars indicate the molar ratio ranges measured in the plumes from Masaya Volcano (Rüdiger et al., 2021). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

background is often almost negligible. Indeed, the abundances of the elements in samples from the summit are 1 to 4 order of magnitude higher than the local background. More difficult is to distinguish between gaseous, soluble-salt and silicate particles sources of the element. The refractory elements correlate perfectly with each other (see correlation coefficient matrix in Table A2; Appendix). Such evidence, coupled with the fact that the refractory elements show EF close to 1, allows us to assume that the relative contribution of dissolved elements can be retrieved with respect to Al as conservative element (this assumption is reasonable when considering that the pH is always very low).

The molar ratios between a couple of elements in rock samples can easily be retrieved from the oxides weight percentages according to:

$$\frac{x}{y} \text{ (molar)} = \frac{CW_x \times n_x \times MW_y}{CW_y \times n_y \times MW_x} \quad (2)$$

where CW_x and CW_y are weight percentages of the oxides containing the elements x and y, n_x and n_y are the subscripts of x and y in the oxide formulas, and MW_x and MW_y are the molecular weight of the oxides.

When plotting Al versus Na, K, Ca, Mg, Fe, Si, Al, Sr, Mn, Be, Rb, Pb, Cu, and Cd (Fig. 5) we can clearly appreciate that refractory elements closely fit the molar ratios in rocks and Pele's hairs while semi-volatile elements are always enriched with a higher dispersion. Among the refractory elements, Si is often depleted, as Si is retained in silicate glass after leaching. Mouné et al. (2007) analyzed Pele's tears collected at Masaya volcano and observed that the Si content was much higher in the outer part than the inner part. The very fast quenching of ejecta produced by magma fragmentation should produce silicate particles with a homogenous composition but the interaction of silicate glass with acidic gases yields to the formation of the siliceous rim. The development of this siliceous rim confirms that the mobility of Si is low under these conditions. Conversely, Mg and Al were found to be depleted in the outer part, testifying to their higher mobility. A similar process was observed by Chemtob and Rossman (2014). They reported results on the alteration of fresh basalts at Kilauea under wet acidic conditions. They described the formation of a SiO_2 coating due to in situ dissolution of near-surface basalt that removes other cations associated with basalt (Na^+ , Ca^{2+} , Mg^{2+} , Al^{3+} , Fe^{3+} , and Ti^{4+}).

We can then calculate the element concentrations corrected for the contribution of the dissolution of silicate particles according to the following equation:

$$C_{i(c)}^p = C_{i(t)}^p - C_{Al(t)}^p \times \frac{C_i^R}{C_{Al}^R} \quad (3)$$

where $C_{i(c)}^p$ is the concentration of the i -th element corrected for the dissolution of silicate particles, $C_{i(t)}^p$ is the total concentration of the i -th element, $C_{Al(t)}^p$ is the concentration of Al, and $\frac{C_i^R}{C_{Al}^R}$ is the molar ratio between the i -th element and Al in rock using data of sample MS1997 in Mouné et al. (2010).

Under the assumption that the main processes responsible for volcanic emissions are lava fragmentation and volatilization and that rain events efficiently scavenge plume particles, the $C_{i(c)}^p$ values represent the relative fraction of each element that has been emitted from the magma as non-silicate particles. We can use these values to retrieve information on the fluid/melt partition coefficients.

The fluid/melt partition coefficient ($D^{f/m}$) is defined as:

$$D_i^{f/m} = \frac{C_i^f}{C_i^m} \quad (4)$$

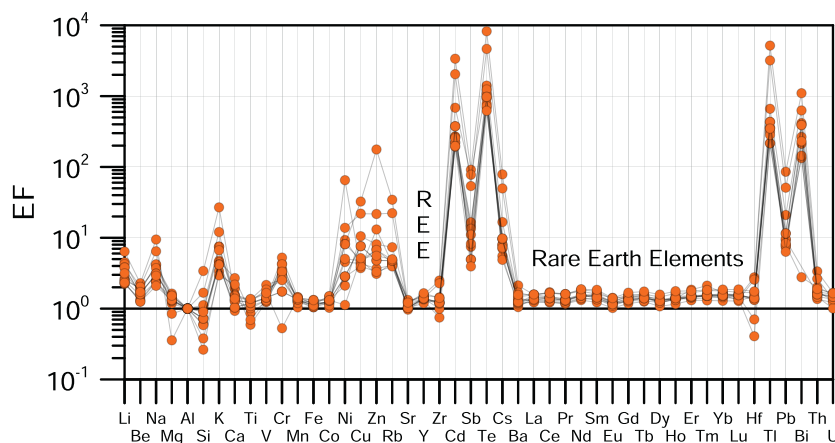


Fig. 4. Enrichment factors normalized to Al for the summit rainwater samples. Data used to normalize are relative to the rock sample MS1997 in Moune (2005) and Moune et al. (2010) except for Li, Cr, Co, Ni, and V, which are from Carr et al. (2014).

where C_i^f and C_i^m indicate the concentration of the element i -th in the fluid and in the melt respectively. The ratios of two semi-volatile elements (e.g. x and y) in the fluid depend on the concentration of those elements in the melt and on the ratio between their partition coefficients according to:

$$\left(\frac{C_x^f}{C_y^f}\right) = \left(\frac{C_x^m}{C_y^m}\right) \times \left(\frac{D_x^{f/m}}{D_y^{f/m}}\right) \text{ and } R_D = \left(\frac{D_x^{f/m}}{D_y^{f/m}}\right) \quad (5)$$

Of course, the corrected concentration values (Eq. (3)) do not directly relate to partition coefficients, because their dissolution in rainwater affects their overall concentration. However, ratios of partition coefficients normalize out this dilution effect. We can therefore derive the ratio of the partition coefficients (R_D) of two elements based on their $C_{i(c)}^p$ values.

Semi-volatile elements (Na, K, Rb, Pb, Cu, and Cd) can be released from volcanoes as gaseous chlorides/sulfides and aerosols (Pennisi et al., 1988; Symonds et al., 1992; Zelenski et al., 2013; Mather, 2015; Henley and Seward, 2018). Their concentrations in plume affected samples thus derive from degassing that produces gaseous and solid halides/sulfides and from the acidic leaching of silicate particles. Following Liotta et al. (2017), we derived R_D with respect to Rb (Fig. 6) to make easily comparable values with previous results obtained at Nyiragongo. Rb, K, and Cu exhibit similar fluid/melt partition coefficients resulting in R_D close to 1 (Fig. 6). Conversely, Na shows a lower fluid/melt partition coefficient with respect to Rb. The high volatility of Cd and Pb is confirmed by their R_D values, 70 and 3 times higher than that of Rb, respectively. In summary, we can define the following volatility scale: Cd > Pb > Rb ≈ K ≈ Cu > Na. The most evident difference with respect to previous results obtained at Nyiragongo (i.e. Pb > Rb > K > Na) is that Pb shows a lower volatility suggesting that partition coefficients could depend on the magma composition, whereas the lower volatility of Na with respect to Rb is confirmed at Masaya. At Erta Ale volcano, based on different sampling methods applied to high temperature fumaroles, Zelenski et al. (2013) observed that alkali metals had EF values (using Mg as reference element) between 31 and 500 with Cs > Rb > K > Na > Li which is consistent with our findings, while chalcophile elements in the range from 276 to almost 10^7 with Cd > Pb. Interestingly, Pb displays a different volatility at Masaya and Erta Ale in spite of the fact that they have lava lakes with very similar magma composition. This could depend on the different oxygen fugacity values. Indeed, de Moor et al. (2013) investigated the relationship between sulfur and oxygen fugacity at Erta Ale and Masaya volcanoes and observed that Erta Ale melts have fO_2 of $\Delta QFM 0.0 \pm 0.3$ while Masaya is more oxidized with fO_2 of $\Delta QFM +1.7 \pm 0.4$. Sossi et al. (2019) observed that the evaporation of moderately volatile elements from silicate melts is highly redox-

dependent and that Pb becomes more volatile with decreasing fO_2 . On the assumption that Na, Rb, K, Cu, and Pb vaporize as the monatomic gas vapor, pressure of $Pb_{(g)}$ is proportional to $fO_2^{-1/2}$ whereas pressure of $Na_{(g)}$, $Rb_{(g)}$, $K_{(g)}$, and $Cu_{(g)}$ is proportional to $fO_2^{-1/4}$, which arises from their different speciation in silicate melts (e.g. Pb^{2+} and Na^+). Therefore, as fO_2 decreases, Pb becomes more volatile relative to Na, K, Rb, and Cu. Andersen et al. (2014) estimated ΔQFM of -2 to -3 for the nephelinite from Nyiragongo volcano. Even if the Nyiragongo volcano has a very different magma composition with respect to Masaya, its much lower oxygen fugacity could reasonably be the cause of the different Pb volatilities observed. However, we cannot exclude that different concentrations of volatile elements in magma play some roles in determining the element volatility. Indeed, volatile trace metals degassing also depend on the availability of S and Cl (Scholtysik and Canil, 2021; Zelenski et al., 2021). Future thermodynamic models could be used to better clarify the dependence of metals volatility on volatile elements content.

We computed R_D for all the elements for which rock concentration was available from Moune et al. (2010) and Carr et al. (2014). We thus defined an overall volatility scale (Fig. 7). The scale highlights the very high volatility of Bi, Cd, Tl, and Te in agreement with previous findings of Symonds et al. (1987), Martin et al. (2012), Zelenski et al. (2013), Liotta et al. (2017) Zelenski et al. (2021). We believe that with respect to the enrichment factors, the ratio of the partition coefficients provides a better evaluation of the relative volatility of the elements. Elements whose concentrations have not been measured in Masaya's rocks are not included in Fig. 7. However, a clear correlation exists between Mo and highly volatile elements such as Te, Cs, Tl, Pb, and Bi (Table A2). We can therefore assume that also Mo behaves as a volatile element as previously observed by Symonds et al. (1987) at Merapi and Poás volcanoes (Martínez Cruz, 2008). Such evidence is in contrast with volatility scales defined based on thermodynamic data (e.g. Allègre et al., 2001) while it matches experimental findings of Sossi et al. (2019). However, it should be mentioned that Allègre et al. (2001) dealt with planetary accretion and the solar nebula under very different settings (fO_2 , fH_2O , total pressure) with respect to volcanic degassing.

Concerning Pb, the average value of Pb/Cl is $1.67 \cdot 10^{-6}$ in rain samples. Assuming that all the emitted gaseous HCl was dissolved in water we can retrieve the Pb/S(t) in the volcanic plume. The S/Cl ratio in the plume range between 0.3 and 2.1 (Rüdiger et al., 2021). If we consider an intermediate value of 1.2 (Martin et al., 2010 observed a S/Cl ratio equal to 2) we compute the Pb/S(gas) of about $1.4 \cdot 10^{-6}$ which is close to the value obtained by Vallelonga and Mather (2003).

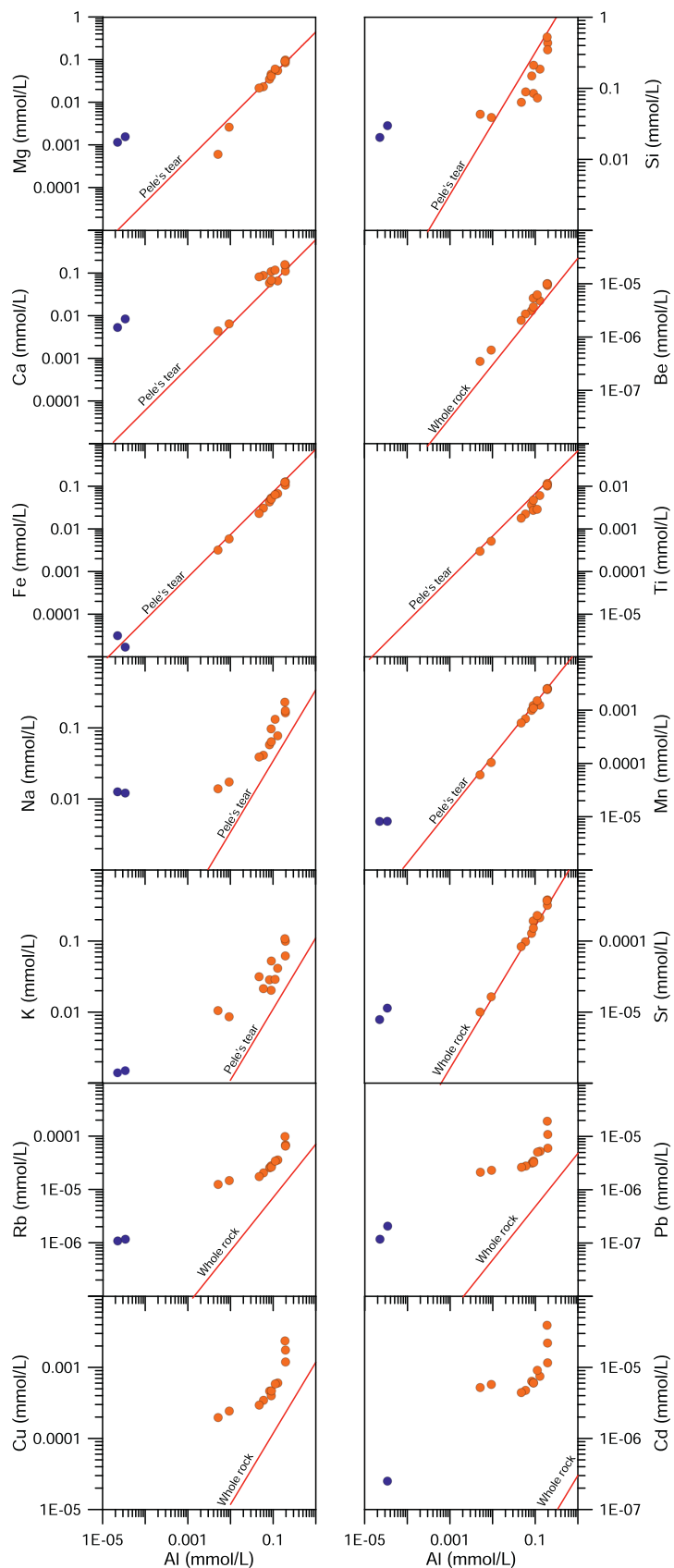
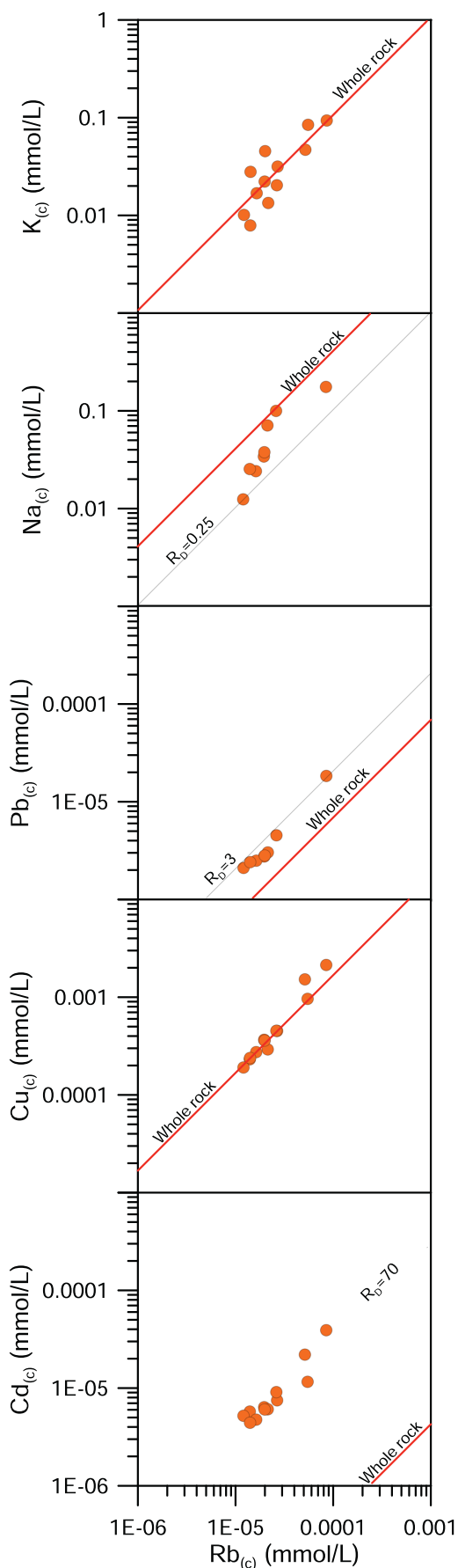


Fig. 5. Al versus Na, K, Ca, Mg, Fe, Si, Sr, Mn, Be, Rb, Pb, Cu, Ti and Cd in rainwater. The molar ratios (red lines) in rock are also shown (whole-rock and Pele's tear data from Mouné et al. (2007, 2010). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



(caption on next column)

Fig. 6. Corrected values (see text for details) of Rb versus corrected values of Na, K, Pb, Cu and Cd in plume-affected rain samples. Molar ratios in rock are also given as a red line (data of sample MS1997 in Mouné et al., 2010). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4.3. Magmatic REE signature in precipitation

The concentrations of REEs are typically determined in magmatic rock samples (e.g. Carr et al., 2007; Mouné et al., 2010). Their incompatible behavior during mineral formation in magmatic bodies makes them useful in evaluating the magma source. REE concentrations in our precipitation samples clearly originate from the dissolution of silicate particles as they show an EF value close to 1 (Fig. 4) and their concentrations closely correlate with refractory elements (Table A2). Our findings are consistent with those of Martin et al. (2012) who observed a refractory behavior of REEs. Similarly, Zelenski et al. (2013) found that REE had a high affinity with particles even if they state that some volatile transport of REE in extremely high-T gases cannot be excluded. Here we highlight that Sossi et al. (2019) showed that REEs are retained in the melt under all experimental conditions they explored (up to 1550 °C) during evaporation of silicate melts.

The chondrite-normalized REE patterns of precipitation samples perfectly mirror that of the rock (Fig. 8). The higher or lower concentration of REEs only depends on the relative amounts of rain and dissolved solid particles. This extraordinary consistency represents a fingerprint that unequivocally confirms that REE in acid precipitation interacting with the Masaya volcanic plume, derive from the dissolution of silicate particles.

5. Conclusions

In this study, we explore the interaction processes occurring during the falling of raindrops through the volcanic plume and further modifications by silicate particle dissolution in the bulk collectors at Masaya volcano. Gaseous emissions, namely HCl, HF, HBr, HI, and SO₂, interact with rainwater to different extents depending on their chemical properties. While we expect that the most acidic gases promptly dissolve in water and dissociate, being detected as conjugate bases (Cl⁻, Br⁻, I⁻), we observed lower Br/Cl ratios than the plume ratios thus suggesting possible HBr conversion to form less soluble Br species. HF and SO₂ involve different processes. HF dissolves silica and strongly interacts with very abundant silicate particles in the plume. Subsequent interaction with rainwater determines the concentration of dissolved F⁻. SO₂ needs time to be oxidized to H₂SO₄ that easily dissociates in water. Oxidation represents a rate limiting step and, as a consequence, the SO₄²⁻/Cl⁻ ratio in rain does not match that of the plume. Refractory elements perfectly fit the molar ratios in rocks while semi-volatile elements are always enriched. Under very acidic conditions, silicate particles dissolve almost isochemically thus leaving a clear signature in rainwater. Once the relative contribution of silicate particle dissolution is computed and subtracted, and assuming that volcanogenic elements are released to the atmosphere through magma fragmentation and volatilization, we defined a relative volatility scale based on this approach. With respect to other volcanoes hosting a lava lake, we observed that Pb is relatively less volatile and suggests degassing at Masaya occurred at a higher oxygen fugacity than Nyiragongo and Erta Ale.

We compared our results with available data relative to the rock composition. Unfortunately, data on As, Se, Mo, Sn are not available for rock. Since a clear correlation exists between Mo and other volatile elements, and because Mo has been increasing in water of acidic volcanic lakes and fumarole condensate of other volcanoes during periods of enhanced magmatic output, we speculate that Mo has a high volatility.

Finally, we found that REEs in rain samples depict the same

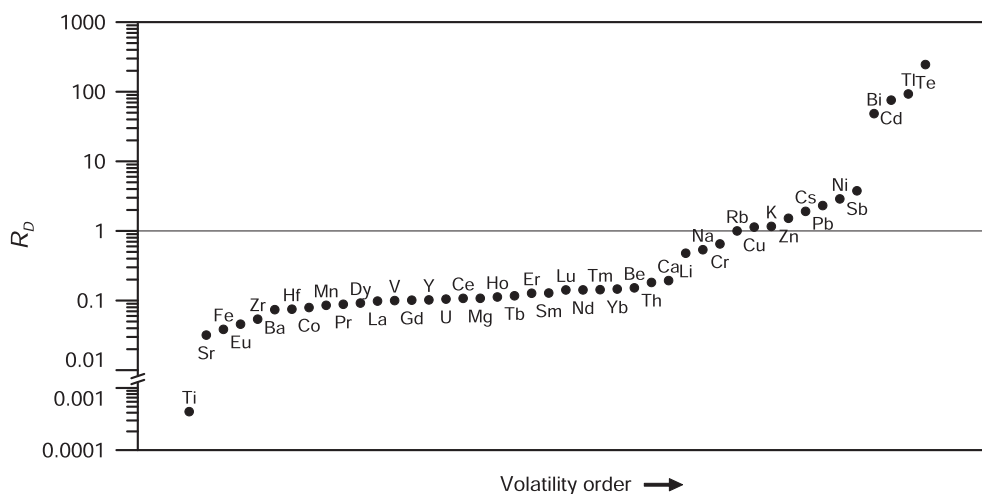


Fig. 7. Volatility scale defined based on the average of R_D values computed versus Rb for rainwater summit samples except for samples from Mirador site.

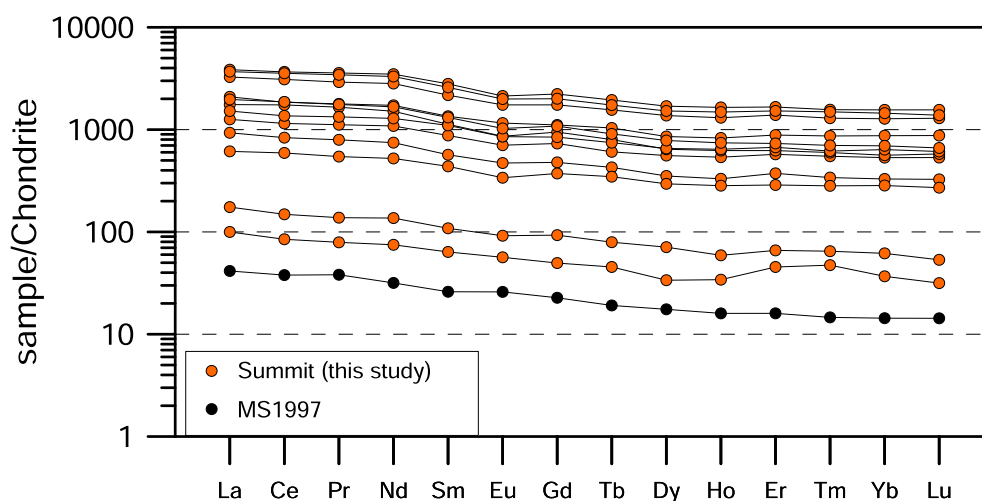


Fig. 8. Chondrite-normalized REE patterns for the precipitation samples. Data relative to bomb sample are also plotted for comparison (sample MS1997 in Mouné et al., 2010).

chondrite-normalized patterns as in the rock, thus confirming their refractory behavior previously argued by Martin et al. (2012). Since the chemical composition of refractory trace elements in summit rain samples perfectly mirrors that of the rocks, we suggest that sampling of plume-affected rain samples could represent an alternative way to explore some geochemical features of lava lakes without direct sampling of the lava or collection of Pele's hair/tears. If rainwater truly is a faithful proxy for magma composition, our study suggests that changes in magma compositions at lava lakes should be identifiable by the monitoring of rain samples.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2021.120562>.

Declaration of Competing Interest

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.

Acknowledgments

The authors are very grateful to the staff members of Istituto Nazionale di Geofisica e Vulcanologia, Sezione di Palermo for their

valuable support in the laboratories. Special thanks to Lorenzo Brusca for ICP analyses and to Vincenzo Prano for his support at the IC laboratory. We also thank the staff members of INETER-Nicaragua who provided logistics and support during field sampling at the Masaya Caldera. M.M.C was supported with funding from Universidad Nacional de Costa Rica and the Costa Rican Law of Emergencies and Risk Prevention N° 8488.

References

- Allègre, C., Manhès, G., Lewin, É., 2001. Chemical composition of the Earth and the volatility control planetary genetics. *Earth Planet. Sci. Lett.* 185, 49–69. [https://doi.org/10.1016/S0012-821X\(00\)00359-9](https://doi.org/10.1016/S0012-821X(00)00359-9).
- Andersen, T., Elburg, M.A., Erambert, M., 2014. Extreme peralkalinity in delhayelite- and andremeyerite-bearing nephelinite from Nyiragongo volcano, East African Rift. *Lithos* 206–207, 164–178. <https://doi.org/10.1016/j.lithos.2014.07.025>.
- Bagnato, E., Aiuppa, A., Andronico, D., Cristaldi, A., Liotta, M., Brusca, L., Miraglia, L., 2011. Leachate analyses of volcanic ashes from Stromboli volcano: a proxy for the volcanic gas plume composition? *J. Geophys. Res. Atmos.* 116, D17204 <https://doi.org/10.1029/2010JD015512>.
- Balagizi, C.M., Kasereka, M.M., Cuoco, E., Liotta, M., 2017. Rain-plume interactions at Nyiragongo and Nyamulagira volcanoes and associated rainwater hazards, East Africa. *Appl. Geochem.* 81, 76–89. <https://doi.org/10.1016/j.apgeochem.2017.03.018>.
- Bekki, 1995. Oxidation of volcanic SO_2 : a sink for stratospheric OH and H_2O . *Geophys. Res. Lett.* 22 (8), 913–916. <https://doi.org/10.1029/95GL00534>.

- Calabrese, S., Aiuppa, A., Allard, P., Bagnato, E., Bellomo, S., Brusca, L., D'Alessandro, W., Parello, F., 2011. Atmospheric sources and sinks of volcanogenic elements in a basaltic volcano (Etna, Italy). *Geochim. Cosmochim. Acta* 75, 7401–7425. <https://doi.org/10.1016/j.gca.2011.09.040>.
- Carr, M.J., Saginor, I., Alvarado, G.E., Bolge, L.L., Lindsay, F.N., Milidakis, K.I., Turrin, B. D., Feigenson, M.D., Swisher III, C.C., 2007. Element fluxes from the volcanic front of Nicaragua and Costa Rica. *Geochim. Geophys. Geosyst.* 8, Q06001 <https://doi.org/10.1029/2006GC001396>.
- Carr, M.J., Feigenson, M.D., Bolge, L.L., Walker, J.A., Gazel, E., 2014. RU_CAGeochem, a database and sample repository for Central American volcanic rocks at Rutgers University. *Geosci. Data J.* 1, 43–48. <https://doi.org/10.1002/gdj3.10>.
- Chakrabarti, R., Basu, A.R., Santo, A.P., Tedesco, D., Vaselli, O., 2009. Isotopic and geochemical evidence for a heterogeneous mantle plume origin of the Virunga volcanics, Western rift, East African Rift system. *Chem. Geol.* 259, 273–289. <https://doi.org/10.1016/j.chemgeo.2008.11.010>.
- Chemtob, S.M., Rossman, G.R., 2014. Timescales and mechanisms of formation of amorphous silica coatings on fresh basalts at Kilauea Volcano, Hawai'i. *J. Volcanol. Geotherm. Res.* 286, 41–54. <https://doi.org/10.1016/j.jvolgeores.2014.08.029>.
- Cuoco, E., Spagnuolo, A., Balagizi, C., De Francesco, S., Tassi, F., Vaselli, O., Tedesco, D., 2013. Impact of volcanic emissions on rainwater chemistry: the case of Mt. Nyiragongo in the Virunga volcanic region (DRC). *J. Geochem. Explor.* 125, 69–79. <https://doi.org/10.1016/j.jgexplo.2012.11.008>.
- De Maria, G., Balducci, G., Guido, M., Piacente, V., de Maria, G., Balducci, G., Guido, M., Piacente, V., 1971. Mass spectrometric investigation of the vaporization process of Apollo 12 lunar samples. *LPSC 2*, 1367.
- de Moor, J.M., Fischer, T.P., Sharp, Z.D., Hilton, D.R., Barry, P.H., Mangasini, F., Ramirez, C., 2013. Gas chemistry and nitrogen isotope compositions of cold mantle gases from Rungwe Volcanic Province, southern Tanzania. *Chem. Geol.* 339, 30–42. <https://doi.org/10.1016/j.chemgeo.2012.08.004>.
- Delmelle, P., Stix, J., Bourque, C.P.A., Baxter, P., Garcia-Alvarez, J., Barquero, J., 2001. Dry deposition and heavy acid loading in the vicinity of Masaya volcano, a major sulfur and chlorine source in Nicaragua. *Environ. Sci. Technol.* 7, 1289–1293. <https://doi.org/10.1021/es000153m>.
- Delmelle, P., Stix, J., Baxter, P., Garcia-Alvarez, J., Barquero, J., 2002. Atmospheric dispersion, environmental effects and potential health hazard associated with the low-altitude gas plume of Masaya volcano, Nicaragua. *Bull. Volcanol.* 64, 423–434. <https://doi.org/10.1007/s00445-002-0221-6>.
- Delmelle, P., Lambert, M., Dufrene, Y., Gerin, P., Óskarsson, N., 2007. Gas/aerosol-ash interaction in volcanic plumes: new insights from surface analyses of fine ash particles. *Earth Planet. Sci. Lett.* 259, 159–170. <https://doi.org/10.1016/j.epsl.2007.04.052>.
- Field, L., Barnie, T., Blundy, J., Brooker, R.A., Keir, D., Lewi, E., Saunders, K., 2012. Integrated field, satellite and petrological observations of the November 2010 eruption of Erta Ale. *Bull. Volcanol.* 74, 2251–2271. <https://doi.org/10.1007/s00445-012-0660-7>.
- Gauthier, P.J., Le Cloarec, M.F., 1998. Variability of alkali and heavy metal fluxes released by Mt. Etna volcano, Sicily, between 1991 and 1995. *J. Volcanol. Geotherm. Res.* 81, 311–326. [https://doi.org/10.1016/S0377-0273\(98\)00002-X](https://doi.org/10.1016/S0377-0273(98)00002-X).
- Google. (2021). Royal Roads University. Retrieved from <https://goo.gl/maps/77irRRBmxtmktbDn9>.
- Hendry, C.D., Berish, C.W., Edgerton, E.S., 1984. Precipitation chemistry at Turrialba, Costa Rica. *Water Resour. Res.* 20, 1677–1684. <https://doi.org/10.1029/WR020i011P01677>.
- Henley, R.W., Seward, T.M., 2018. Gas–solid reactions in arc volcanoes: ancient and modern. *Rev. Mineral. Geochem.* 84, 309–349. <https://doi.org/10.2138/RMG.2018.84.9>.
- Johnson, N., Parnell, R.A., 1986. Composition, distribution and neutralization of 'acid rain' derived from Masaya volcano Nicaragua. *Tellus* 38 (B), 106–117. <https://doi.org/10.3402/tellusb.v38i2.15086>.
- Liotta, M., Brusca, L., Grassa, F., Inguaggiato, S., Longo, M., Madonia, P., 2006. Geochemistry of rainfall at Stromboli volcano (Aeolian Islands): Isotopic composition and plume-rain interaction. *Geochim. Geophys. Geosyst.* 7, Q07006 <https://doi.org/10.1029/2006GC001288>.
- Liotta, M., Shamavu, P., Scaglione, S., D'Alessandro, W., Bobrowski, N., Bruno, Giuffrida G., Tedesco, D., Calabrese, S., 2017. Mobility of plume-derived volcanogenic elements in meteoric water at Nyiragongo volcano (Congo) inferred from the chemical composition of single rainfall events. *Geochim. Cosmochim. Acta* 217, 254–272. <https://doi.org/10.1016/j.gca.2017.08.001>.
- Martin, R.S., Sawyer, G.M., Spampinato, L., Salerno, G.G., Ramirez, C., Ilyinskaya, E., Witt, M.L.I., Mather, T.A., Watson, I.M., Phillips, J.C., Oppenheimer, C., 2010. A total volatile inventory for Masaya Volcano, Nicaragua. *J. Geophys. Res.* 115, B09215 <https://doi.org/10.1029/2010JB007480>.
- Martin, R.S., Sawyer, G.M., Day, J.A., Leblond, J.S., Ilyinskaya, E., Oppenheimer, C., 2012. High-resolution size distributions and emission fluxes of trace elements from Masaya volcano, Nicaragua. *J. Geophys. Res. Solid Earth* 117, 1–12. <https://doi.org/10.1029/2012JB009487>.
- Martínez Cruz, M., 2008. *Geochemical Evolution of the Acid Crater Lake of Poás Volcano: Insights Into Volcanic-Hydrothermal Processes*. PhD dissertation. Utrecht University, the Netherlands, p. 109.
- Mather, T.A., 2008. Volcanism and the atmosphere: The potential role of the atmosphere in unlocking the reactivity of volcanic emissions. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* 366, 4581–4595. <https://doi.org/10.1098/rsta.2008.0152>.
- Mather, T.A., 2015. Volcanoes and the environment: Lessons for understanding Earth's past and future from studies of present-day volcanic emissions. *J. Volcanol. Geotherm. Res.* 304, 160–179. <https://doi.org/10.1016/j.jvolgeores.2015.08.016>.
- Mather, T.A., Allen, A.G., Oppenheimer, C., Pyle, D.M., McGonigle, A.J.S., 2003. Size-resolved characterisation of soluble ions in the particles in the tropospheric plume in Masaya volcano, Nicaragua: Origins and plume processing. *J. Atmos. Chem.* 46, 207–237. <https://doi.org/10.1023/A:1026327502060>.
- Mather, T.A., Oppenheimer, C., Allen, A.G., McGonigle, A.J.S., 2004. Aerosol chemistry of emissions from three contrasting volcanoes in Italy. *Atmos. Environ.* 38, 5637–5649. <https://doi.org/10.1016/j.atmosenv.2004.06.017>.
- Mather, T.A., Witt, M.L.I., Pyle, D.M., Quayle, B.M., Aiuppa, A., Bagnato, E., Martin, R.S., Sims, K.W.W., Edmonds, M., Sutton, A.J., Ilyinskaya, E., 2012. Halogens and trace metal emissions from the ongoing 2008 summit eruption of Kilauea volcano, Hawaii. *Geochim. Cosmochim. Acta* 83, 292–323. <https://doi.org/10.1016/j.gca.2011.11.029>.
- Moune, S., 2005. Volatils mineurs (S, Cl, F) et éléments traces dans les magmas pré-éruptifset les gaz volcaniques. Etude des processus de dégazage magmatique sur les volcans Hekla (Islande) et Masaya (Nicaragua). *Geochimie. Université Blaise Pascal - Clermont-Ferrand II*. <https://tel.archives-ouvertes.fr> (accession No.: tel-00011542).
- Moune, S., Faure, F., Gauthier, P.-J., Sims, K.W.W., 2007. Pele's hairs and tears: natural probe of volcanic plume. *J. Volcanol. Geotherm. Res.* 164, 244–253. <https://doi.org/10.1016/j.jvolgeores.2007.05.007>.
- Moune, S., Gauthier, P.-J., Delmelle, P., 2010. Trace elements in the particulate phase of the plume of Masaya Volcano, Nicaragua. *J. Volcanol. Geotherm. Res.* 193, 232–244. <https://doi.org/10.1016/j.jvolgeores.2010.04.004>.
- Pennisi, M., Le Cloarec, M.F., Lambert, G., Le Rouley, J.C., 1988. Fractionation of metals in volcanic emissions. *Earth Planet. Sci. Lett.* 88, 284–288. [https://doi.org/10.1016/0012-821X\(88\)90085-4](https://doi.org/10.1016/0012-821X(88)90085-4).
- Perrin, D.D., 1969. *Dissociation Constants of Inorganic Acids and Bases in Aqueous Solution*, 1969. Butterworths, London.
- Prano, V., Liotta, M., 2017. Precision e accuratezza nella determinazione dei costituenti maggiori in soluzione acquosa mediante cromatografia ionica: stime per i cromatografi Dionex ICS-1100 utilizzati presso la Sezione INGV di Palermo. In: *Rapp. Tec. INGV*, 390, pp. 1–22. <https://doi.org/10.13127/rpt/390>.
- Rose, C., Rissanen, M., Iyer, S., Duplissy, J., Yan, C., Nowak, J., Colomb, A., Dupuy, R., He, X.-C., Lampilahti, J., Tam, Y.J., Wimmer, D., Metzger, J.-M., Tulet, P., Brioude, J., Planche, C., Kulmala, M., Sellegri, K., 2020. Investigation of several proxies to estimate sulfuric acid concentration in volcanic plume conditions. *Atmos. Chem. Phys. Discuss.* 1–28 <https://doi.org/10.5194/acp-21-4541-2021>.
- Rüdiger, J., Gutmann, A., Bobrowski, N., Liotta, M., de Moor, J.M., Sander, R., Dinger, F., Tiritz, J.-L., Ibarra, M., Saballos, A., Martínez, M., Mendoza, E., Ferruffino, A., Stix, J., Valdés, J., Castro, J.M., Hoffmann, T., 2021. Halogen activation in the plume of Masaya volcano: field observations and box model investigations. *Atmos. Chem. Phys.* 21, 3371–3393. <https://doi.org/10.5194/acp-21-3371-2021>.
- Scholtysik, R., Canil, D., 2021. The effects of S, Cl and oxygen fugacity on the sublimation of volatile trace metals degassed from silicate melts with implications for volcanic emissions. *Geochim. Cosmochim. Acta* 301, 141–157. <https://doi.org/10.1016/j.gca.2021.02.018>.
- Seinfeld, J.H., Pandis, S.N., 2006. *Atmospheric Chemistry and Physics*, 2nd ed. John Wiley and Sons, New York.
- Sossi, P.A., Klemme, S., O'Neill, H.S.C., Berndt, J., Moynier, F., 2019. Evaporation of moderately volatile elements from silicate melts: experiments and theory. *Geochim. Cosmochim. Acta* 260, 204–231. <https://doi.org/10.1016/j.gca.2019.06.021>.
- Spilliaert, N., Allard, P., Métrich, N., Sobolev, A., 2006a. Melt inclusion record of the conditions of ascent, degassing and eruption of primitive alkali basalt during the powerful 2002 flank eruption of Mount Etna. *J. Geophys. Res.* 111 (B4), B04203. <https://doi.org/10.1029/2005JB003934>.
- Spilliaert, N., Métrich, N., Allard, P., 2006b. S–Cl–F degassing pattern of water rich alkali basalt: modelling and relationship with eruption styles of Mount Etna volcano. *Earth Planet. Sci. Lett.* 248, 772–786.
- Storey, W.C., 1973. Volatilization studies on a terrestrial basalt and their applicability to volatilization from the lunar surface. *Nat. Phys. Sci.* 241, 154–157. <https://doi.org/10.1038/physci241154a0>.
- Symonds, R.B., Rose, W.I., Reed, M.H., Lichte, F.E., Finnegan, D.L., 1987. Volatilization, transport and sublimation of metallic and non-metallic elements in high temperature gases at Merapi Volcano, Indonesia. *Geochim. Cosmochim. Acta* 51, 2083–2101. [https://doi.org/10.1016/0016-7037\(87\)90258-4](https://doi.org/10.1016/0016-7037(87)90258-4).
- Symonds, R.B., Reed, M.H., Rose, W.I., 1992. Origin, speciation, and fluxes of trace-element gases at Augustine volcano, Alaska: insights into magma degassing and fumarolic processes. *Geochim. Cosmochim. Acta* 56, 633–657. [https://doi.org/10.1016/0016-7037\(92\)90087-Y](https://doi.org/10.1016/0016-7037(92)90087-Y).
- Vallelonga, P., Mather, T.A., 2003. Lead (Pb) fluxes and Pb isotopic compositions from Masaya Volcano, Nicaragua. *Atmos. Environ.* 37, 4453–4460. [https://doi.org/10.1016/S1352-2310\(03\)00580-6](https://doi.org/10.1016/S1352-2310(03)00580-6).
- Walker, J.A., Williams, S.N., Kalamarides, R.I., Feigenson, M.D., 1993. Shallow open-system evolution of basaltic magma beneath a subduction zone volcano: the Masaya Caldera Complex, Nicaragua. *J. Volcanol. Geotherm. Res.* 56, 379–400. [https://doi.org/10.1016/0377-0273\(93\)90004-B](https://doi.org/10.1016/0377-0273(93)90004-B).
- Welz, O., Savee, J.D., Osborn, D.L., Basu, S.S., Percival, C.J., Shallcross, D.E., Taatjes, C. A., 2012. Direct kinetic measurements of Criegee Intermediate (CH₂O₂) formed by reaction of CH₂I with O₂. *Science* 335, 204–207. <https://doi.org/10.1126/science.1213229>.
- Wittmer, J., Bobrowski, N., Liotta, M., Giuffrida, G., Calabrese, S., Platt, U., 2014. Active alkaline traps to determine acidic-gas ratios in volcanic plumes: sampling techniques and analytical methods. *Geochim. Geophys. Geosyst.* 15, 2797–2820. <https://doi.org/10.1002/2013GC005133>.
- Wolff-Boenisch, D., Gislason, S.R., Oelkers, E.H., 2004. The effect of fluoride on the dissolution rates of natural glasses at pH 4 and 25 °C. *Geochim. Cosmochim. Acta* 68, 4571–4582. <https://doi.org/10.1016/j.gca.2004.05.026>.

- Zelenski, M.E., Fischer, T.P., de Moor, J.M., Marty, B., Zimmermann, L., Ayalew, D., Nekrasov, A.N., Karandashev, V.K., 2013. Trace elements in the gas emissions from the Erta Ale volcano, Afar, Ethiopia. *Chem. Geol.* 357, 95–116. <https://doi.org/10.1016/j.chemgeo.2013.08.022>.
- Zelenski, M., Simakin, A., Taran, Y., Kamenetsky, V.S., Malik, N., 2021. Partitioning of elements between high-temperature, low-density aqueous fluid and silicate melt as derived from volcanic gas geochemistry. *Geochim. Cosmochim. Acta* 295, 112–134. <https://doi.org/10.1016/j.gca.2020.12.011>.
- Zurek, J., Moune, S., Williams-Jones, G., Vigouroux, N., Gauthier, P.J., 2019. Melt inclusion evidence for long term steady-state volcanism at Las Sierras-Masaya volcano, Nicaragua. *J. Volcanol. Geotherm. Res.* 378, 16–28. <https://doi.org/10.1016/j.jvolgeores.2019.04.007>.