Chemical variability in volcanic gas plumes and fumaroles along the East African Rift System: new insights from the Western Branch

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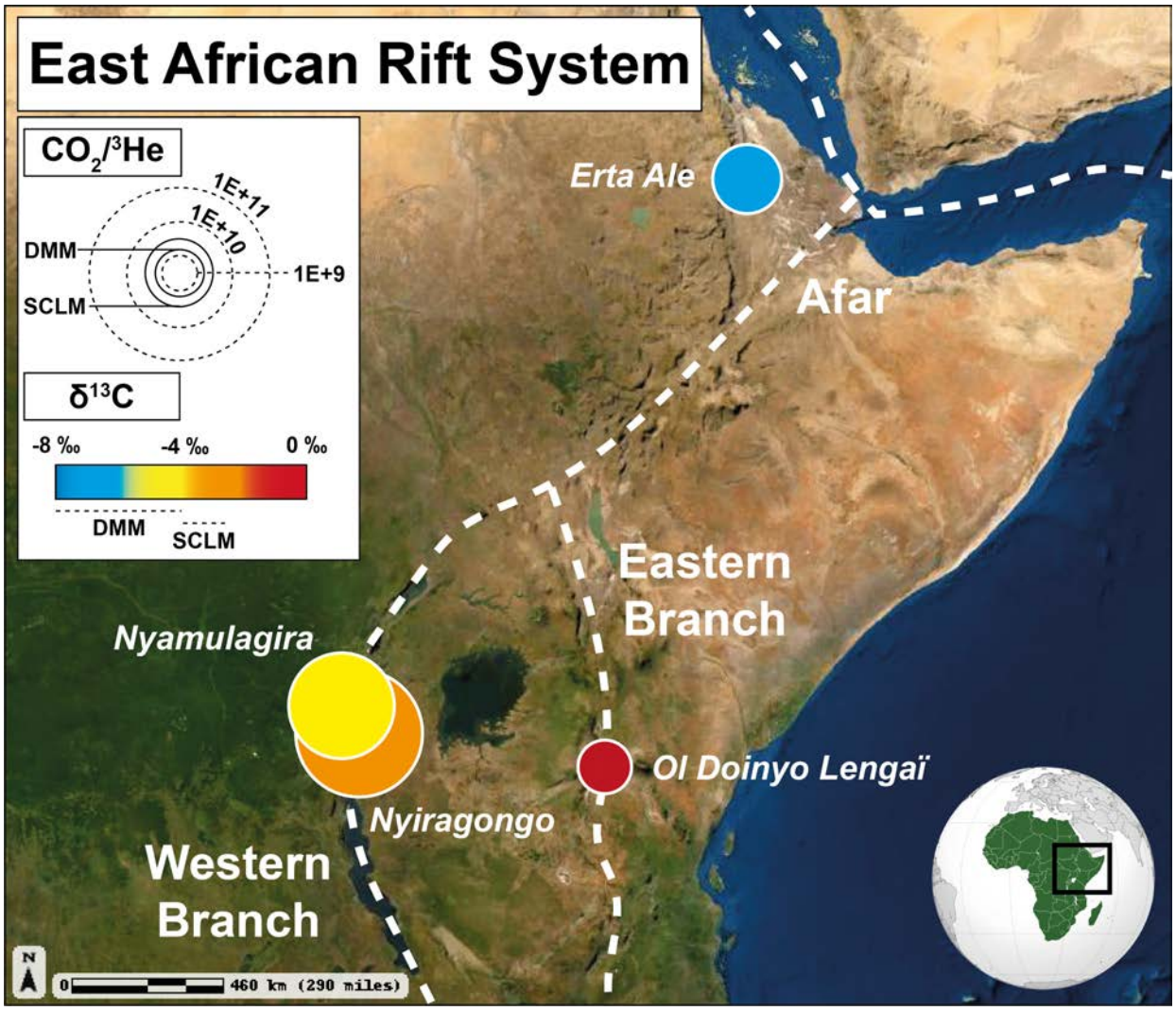
Highlights:

- No evidence in volcanic gases of a high $^{3}He/^{4}He$ mantle plume beneath the VVP
- Major contribution of a lithospheric mantle source beneath the VVP
- Clear evidence of carbonate metasomatism along the Western Branch of the rift

Abstract

The origin of magmatic fluids along the East African Rift System (EARS) is a long-lived field of debate in the scientific community. Here, we investigate the chemical composition of the volcanic gas plume and fumaroles at Nyiragongo and Nyamulagira (Democratic Republic of Congo), the only two currently erupting volcanoes set on the Western Branch of the rift. Our results are in line with earlier conceptual models proposing that volcanic gas emissions along the EARS mainly reflect variable contributions of either a Sub-Continental Lithospheric Mantle (SCLM) component or a Depleted Morb Mantle (DMM) component, and deeper fluid. At Nyiragongo and Nyamulagira, our study discards a major contribution of a high $^{3}He/^{4}He$ mantle plume component in the genesis of volcanic fluids beneath the area. High $CO_2/^{3}He$ in fumaroles of both volcanoes is thought to reflect carbonate metasomatism in the lithospheric mantle source. As inferred by previous results obtained on the lava chemistry, this carbonate metasomatism would be more pronounced beneath Nyiragongo. This supports the idea of the presence of distinct metasomes within the lithospheric mantle beneath the Western Branch of the rift.

Graphical abstract



Keywords:

East African Rift System, volcano, gas chemistry

1 Introduction

The East African Rift System (EARS) is the longest active continental rift system on Earth and is extensively studied by the scientific community focused on plate tectonics and geodynamics (e.g., Rooney et al., 2020) (Fig. 1). In the last few years, the role of continental rifting on the global carbon budget and climate dynamics has also been revisited (Wong et al., 2019). Large diffusive CO_2 emissions together with the unusual abundance of carbon-rich melts are among many evidences of the high outflux of volatile elements along the EARS. However, the origin of volatile elements beneath the EARS remains understudied with respect to other geodynamical contexts (Rooney et al., 2020). It has been firstly proposed that only the Afar-Ethiopian part of the EARS shows the contribution of a deep common ('C'-type) mantle plume as revealed by the abundance of primordial helium ($^3He/^4He$ up to 19.6 Ra and mostly >9 Ra) (Pik et al., 2006; Darrah et al., 2013; O'Connor et al., 2019; Rooney et al., 2020). The magmatic activity along the Eastern and Western branches of the rift marked by lower $^3He/^4He$ values (<9 Ra) were ascribed to the contribution of either a Depleted Morb Mantle 'DMM' (Fischer et al., 2009) or second-order type mantle plumes upwelling in the shallow mantle (<500 km) (Pik et al., 2006). The discovery of ratios as high as 15 Ra in the Rungwe Volcanic Province in the South of Tanzania (Barry et al., 2013) upset this theory and has favored the emergence of a new model in which gas emissions along the whole EARS testify various extents of mixing between two components (Halldorsson et al., 2014; O'Connor et al., 2019): (1) a deep Common ('C'-type) mantle plume (cf. the "African Superplume") and (2) the Sub-Continental Lithospheric Mantle 'SCLM' (De Moor et al., 2013; Lee et al., 2017).

A field survey in the Virunga Volcanic Province (Democratic Republic of Congo) in 2020 allowed gas collection from volcanic gas plumes (large quantity of volcanic gases that disperse and dilute in the atmosphere) and fumaroles (vents through which steam and volcanic gases are emitted) at Nyiragongo and Nyamulagira (Fig. 1), the only two currently erupting volcanoes on the Western Branch of the EARS (see Methods in Supplementary Information). Based on the first chemical characterization of the fumaroles at Nyamulagira, we explore here the current geochemical variability of gas emissions in this part of the Virunga Volcanic Province. By compiling previous chemical data obtained from fumaroles and volcanic gas plumes only, at other persistently active volcanoes along the EARS, we investigate the spatial variability of geochemical markers in volcanic gaseous emissions along the EARS (Fig. 2).

2 Samples and Methods

The chemical characterization of volcanic gas plumes was performed by using a Multicomponent Gas Analyzer System (MultiGAS) designed at the Istituto Nazionale di Geofisica e Vulcanologia – Sezione di Palermo (INGV Palermo) (Aiuppa et al., 2006; Liuzzo et al., 2013). The instrument allows the collection of H_2O, CO_2 and SO_2 contents in the plume with a 1 Hz acquisition frequency. Two acquisition periods (>30 minutes) were realized at Nyamulagira on February 4 and 6, 2020. Two other series of measurements were obtained at Nyiragongo on February 12, 2020 (Fig. 1c, d). Time series were then postprocessed to calculate CO_2/SO_2 and H_2O/CO_2 ratios with a typical uncertainty <10%. Only ratios with a r-squared >0.7 on a period greater than 5 minutes were considered and averaged to obtain final values for each volcanic gas plume (Table S-1).

One fumarolic gas sample (F2) was collected on February 4, 2020, within the Nyamulagira summit crater with outlet temperature of 84°C (Fig. 1d). Glass samplers were used in line with a 50 cm stainless-steel tube and Dewar glass tubes (Vaselli et al., 2006). Similarly, two fumarolic gas samples (F1-A & F1-B) were collected on February 12 and 13, 2020, on the second platform within the Nyiragongo summit crater (for a description of the summit crater see e.g. Burgi et al., 2020) with outlet temperature of 82°C (Fig. 1c). Collected gas samples were then analyzed at the INGV Palermo for their contents in major and minor gaseous species as well as for the isotopic composition of noble gases (^{3}He, ^{4}He, ^{20}Ne, ^{40}Ar, ^{38}Ar, ^{36}Ar) and their relative ratios, and few other stable isotopes ($\delta^{13}C$ of CO_2) (Table S-2). Content in major and minor gaseous species in glass samplers was analyzed by the use of a gas chromatograph (GC, Agilent 7890 equipped with PPU and MS5A columns) associated with a MicroGC module (equipped with a PPU column) and a double detector (TCD and FID) using argon as carrier gas. The analytical errors were < 3%. The abundances and isotope compositions of He were determined by a split flight tube mass spectrometer (Helix SFT-GVI). Neon abundance and isotope composition (^{20}Ne) was determined by a Helix MC Plus Thermo. The abundances and isotope compositions of Ar were measured in a multicollector mass spectrometer (Helix MC-GVI). The analytical errors of the He, Ne, and Ar-isotope analyses were less than 0.4%, 0.06% and 0.2%, respectively. Analysis of carbon isotopes were obtained with a Thermo Delta Plus XP CF-IRMS coupled with a Thermo TRACE Gas Chromatograph (GC) and a Thermo GC/C III interface. The analytical error on $\delta^{13}C$ are <0.1‰. The analytical procedure and correction for air-contamination of noble gases are the same as the ones described in Boudoire et al. (2020). In particular, the so-called magmatic-derived $^{40}Ar^{*}$ was calculated accordingly with the following formula that assumes that all the measured ^{36}Ar is of atmospheric origin:

$$40Ar^{*} = 40Ar_{m} - \left(\frac{40Ar}{36Ar}\right)_{air} \times 36Ar_{m}$$

where $^{40}Ar^{*}$ represents the corrected ^{40}Ar ($^{40}Ar/^{36}Ar$ = 295.5), and the "m" subscript indicates "measured". In the figures (Fig. 2, 3, 4, 5), the analytical uncertainty on laboratory measurements is less than the size of the symbols.

Rain gauge collectors were deployed (i) beneath the volcanic plume at Nyamulagira (less than <500 m distance to the plume emission center) during the field mission and (ii) at the Observatoire Volcanologique de Goma more than 20 km further downwind (more details of the sampling procedure are available in Calabrese et al. (2011)). Rainwater samples were collected to investigate plume-rain interaction and define a Local Meteoric Water Line (LMWL) based on $\delta^{18}O$ and δD of H_2O. Stable isotopes for H_2O in both condensates from one fumarole (F3) at Nyamulagira (Table S-2) and rainwaters (Table S-3) were analyzed at the INGV – Osservatorio Vesuviano by means of a near-infrared laser analyzer (Picarro L2130i) using WS-CRDS (wavelength scanned cavity ring down spectroscopy) technique (analytical errors are: $\delta D \pm 0.5$‰, $\delta^{18}O \pm 0.08$‰; data are reported vs. V-SMOW) (see Caliro et al. (2015) for details about the analytical procedure). It was not possible to collect a condensate from F2 at Nyamulagira. Consequently, isotopic values in this study refer to the two condensates collected from a high-temperature (>1000 °C) fumarole (F3) for which, in turn, we had problems collecting the gas phase. Expected $\delta^{18}O$ value in local rain was calculated from the equation of Bowen & Wilkinson

(2002) with a latitude of 1° and an altitude of 3000 m in accordance with the geographic position of the Nyamulagira volcano.

Previous data obtained in volcanic gas plumes and fumaroles at persistently active volcanoes along the EARS are compiled from Gerlach (1982), Oppenheimer et al. (2002), Pik et al. (2006), Sawyer et al. (2008a,b), Fischer et al. (2009), Tedesco et al. (2010), Bobrowski et al. (2016, 2017), Boucher et al. (2018) and Mollex et al. (2018). The composition of the end-members used to define the mixing curves are defined from the following literature: DMM (Sheppard & Epstein, 1970; Gautheron & Moreira, 2002; Zelenski & Taran, 2011; Clog et al., 2013; Barry et al. 2013; Hallis et al., 2015; Rizzo et al., 2018), African Superplume (Pik et al., 2006; Darrah et al., 2013), SCLM (Gautheron & Moreira, 2002; Rizzo et al., 2018), Continental Crust (Zelenski & Taran, 2011; Taran & Zelenski, 2015), Oceanic Crust (Zelenski & Taran, 2011; Barry et al. 2013; Taran & Zelenski, 2015), Limestone (Barry et al. 2013), Sediments (Zelenski & Taran, 2011; Barry et al. 2013), Mantle carbonates (Harmer, 1999; Casola et al., 2020; Carnevale et al., 2021), Air and ASW (Zelenski & Taran, 2011).

3 Results

MultiGAS measurements in volcanic gas plumes performed in February 2020 reveal an average CO_2/SO_2 ratio of 22±8.4 and 15.5±5.7 and an average H_2O/CO_2 ratio of 1.9±0.2 and 12.4±6.3 at Nyiragongo and Nyamulagira, respectively (Fig. 2a). At Nyiragongo, CO_2/SO_2 values are higher than FTIR measurements performed in the volcanic gas plume in 2005-2007 (CO_2/SO_2 = 5.1±0.1; H_2O/CO_2 = 3.0±0.2; Sawyer et al., 2008a). At Nyamulagira, CO_2/SO_2 values are similar to those obtained in the volcanic gas plume in 2014 with the same instrument but with a lower H_2O/CO_2 ratio, on average (CO_2/SO_2 = 12.1±0.3; H_2O/CO_2 = 16.8±0.1; Bobrowski et al., 2017). Current and previous data show that the range of CO_2/SO_2 values at Nyamulagira (9.7-21.1) falls in the range of values measured at Nyiragongo (5.0-29.1). Meanwhile, the range of H_2O/CO_2 values is clearly higher at Nyamulagira (9.6-19.6) than at Nyiragongo (1.1-3.2). At larger scale, the ratios obtained for the two erupting volcanoes of the Western branch of the EARS range between two endmembers: Erta Ale and Ardoukoba in the Afar (CO_2/SO_2 = 0.2-1.9; H_2O/CO_2 = 3.8-25.6; Gerlach, 1982; Sawyer et al., 2008b) and Ol Doinyo Lengaï on the Eastern branch of the EARS (CO_2/SO_2 = 3830; H_2O/CO_2 = 3.1; Oppenheimer et al., 2002).

N_2/He and N_2/Ar in fumaroles at Nyiragongo (F1-A and F1-B) range between 1885-1980 and 86-91, respectively. Higher values are found in fumarole (F2) at Nyamulagira with N_2/He = 6814 and N_2/Ar = 93. These values fall very well within the range expected for a mixture between either a DMM or a continental crust component and the air (Fig. 2b). They are intermediate between those measured at Erta Ale and Ol Doinyo Lengaï.

Helium isotopes are indistinguishable in fumaroles of both volcanoes with R/Ra in the range 7.0-7.3 at Nyiragongo and 7.2 at Nyamulagira (Fig. 3a). These values set for both volcanoes of the Virunga Volcanic Province are lower than those observed in the Afar region (R/Ra > 10.9; Boucher et al., 2018; Darrah et al., 2013) but comparable to those of the Ol Doinyo Lengaï (R/Ra = 6.6-7.8; Fischer et al., 2009; Mollex et al., 2018). They are at the limit between the lower range of DMM values (R/Ra = 8±1) and the upper range of the SCLM (R/Ra = 6.1±0.9; Tedesco & Nagao, 1996; Gautheron & Moreira, 2002). $^4He/^{40}Ar^*$ ranges from 0.83 at Nyamulagira up to 1.24-1.41 at Nyiragongo, which is in accordance with previous measurements (1.02-1.20; Tedesco et al., 2010). These values are slightly higher than those measured at Ol Doinyo Lengaï (0.45-0.76). Overall, as suggested at Ol Doinyo Lengaï (Fischer et al., 2009), the range of $^4He/^{40}Ar^*$ values

measured at Nyamulagira and Nyiragongo supports the assumption that the measured volatile compositions are restrictively affected by magma degassing.

Carbon isotopes measured in the fumaroles of both volcanoes are more variable (Fig. 3b). At Nyiragongo, $\delta^{13}C$ of CO_2 range from -3.7 to -3.9 ‰ and are similar to previous measurements (from -3.5 to -4.0 ‰; Tedesco et al., 2010). More negative values are measured at Nyamulagira ($\delta^{13}C$ = -5.2 ‰ in F2). With respect to preexisting measurements performed along the EARS, $\delta^{13}C$ values at Nyiragongo are close to those of Ol Doinyo Lengaï (from -2.4 to -4.0 ‰; Fischer et al., 2009) slightly more positive than typical DMM values (-6±2 ‰; Sano & Marty, 1995) and closer to the European SCLM values (-3.5 ‰; Bräuer et al., 2016; Rizzo et al., 2018). $\delta^{13}C$ values at Nyamulagira are closer to those measured at Erta Ale (from -6.3 to -6.8 ‰; Boucher et al., 2018) and fall in the range of DMM values.

$\delta^{18}O$ and δD measurements of H_2O of rainwaters collected less than 500 m-far from the plume emission center at Nyamulagira and at the Observatoire Volcanologique de Goma (more than 20 km-further) show a well-marked linear correlation ($\delta D = 8.08\ \delta^{18}O + 20.07$; $R^2 = 0.996$), parallel to the Global Meteoric Water Line (GMWL), and could be representative of the Local Meteoric Water Line (LMWL) (Fig. 4). In this respect, the calculated local rain should have an isotopic composition of $\delta^{18}O$ = -11.1 ‰ and δD = -69.4 ‰ (Bowen & Wilkinson, 2002). $\delta^{18}O$ and δD measurements of H_2O performed in the condensate fraction of the Nyamulagira fumaroles (only) range from 7.2 to 8.4 ‰ and from -34.4 to -34.7 ‰, respectively. These values are far from the LMWL and quite similar to SCLM inferred values ($\delta^{18}O$ from 5 to 8 ‰ and δD from -68 to -56 ‰ or from -42 to -32 ‰; Taran & Zelenski, 2015).

4. Discussion

4.1. Contribution of mantle components in the genesis of magmatic fluids beneath the Virunga Volcanic Province

Recent attempts to describe the geochemical variability along the EARS, especially in gaseous emissions, refer mainly to various extents of mixing between a deep Common ('C'-type) mantle plume (cf. the "African Superplume") and a SCLM component (De Moor et al., 2013; Halldorsson et al., 2014; Lee et al., 2017; Mollex et al., 2018; O'Connor et al., 2019). Within this frame of reference, measurements obtained in the Afar region (Erta Ale, Dallol) are ascribed to a greater contribution of the mantle plume (Darrah et al., 2013; Boucher et al., 2018) whereas the activity on the Eastern Branch (Ol Doinyo Lengaï) is thought to represent the predominant contribution of the SCLM in the genesis of magmatic fluids (Mollex et al., 2018; Lee et al., 2017).

Within the Western Branch of the EARS, Rc/Ra in the range 7.1-7.5 at both Nyiragongo and Nyamulagira volcanoes may reflect (i) a DMM signature (8±1) or (ii) a SCLM-like signature (6.1±0.9) marked by a slight enrichment in ^3He (Fig. 3a). $\delta^{13}C$ values of CO_2 at Nyiragongo (Fig. 3b) and $\delta^{18}O$ and δD measurements of H_2O at Nyamulagira appear slightly different to what would be expected in the case of a contribution of the DMM (Fig. 4). The composition of the volcanic gas plumes (H_2O – CO_2 – S_t; Fig. 2a) at both Nyamulagira and Nyiragongo is also significantly different from that measured during the 1978 Ardoukoba eruption fed by E-MORB magma (Vigier et al., 1999). Conversely, $\delta^{13}C$ value of CO_2 at Nyamulagira ($\delta^{13}C$ = -5.2 ‰; Fig. 3b) falls in the typical range of DMM values (-6±2 ‰; Sano & Marty, 1995): this peculiarity observed at Nyamulagira will be discussed later. Although we cannot exclude with certainty the contribution of a DMM source beneath the province, our results better suggest a contribution of the SCLM in the genesis of magmatic fluids similar to what was described for the Eastern Branch of the EARS (Mollex et al., 2018; Lee et al., 2017). This assumption match with previous conclusions from petrological investigations along the Western Branch (Rosenthal et al., 2009; Rooney et al., 2020).

Importantly, our results confirm previous conclusions made along the Western Branch of the EARS (Tedesco et al., 2010; Rooney et al., 2020) that discard a predominant contribution of high $^{3}He/^{4}He$ mantle plumes in the genesis of magmatic fluids there. Nevertheless, the involvement of deeper ^{3}He-rich mantellic fluids may provide a reasonable explanation to the slight enrichment in primordial helium (^{3}He) in gaseous emissions at both Nyiragongo (Rc/Ra = 7.1-7.4 and up to 8.7 in previous studies) and Nyamulagira (Rc/Ra = 7.5) with respect to typical SCLM values (6.1±0.9). A similar ^{3}He-enrichment was recently measured in fluid inclusions in calcite (Rc/Ra = 9.6) from carbonatites in Uganda and is thought reflecting a rapid ascent of carbonatitic magma from depth across the SCLM (Benko et al., 2021). Deeper mantle reservoirs at the origin of such an enrichment in ^{3}He in the SCLM may involve: an undegassed archetypal mantle plume like the African Superplume (Darrah et al., 2013), a partially degassed mantle plume component (degassed plume head or degassed material through lateral channeling of the plume; Darrah et al., 2013) as proposed in the Afar (Erta Ale; Darrah et al., 2013; Boucher et al., 2018) and/or a depleted mantle component (see Rooney et al. (2020) for a review). Further work, especially on the geochemical characterization of the SCLM beneath the province, is required to distinguish the respective contributions of these components in the genesis of magmatic fluids along the Western Branch of the EARS.

4.2. Carbon enrichment tracked by gaseous emissions

The $CO_2/^{3}He$ values of the fumaroles in the Virunga Volcanic Province strongly differs from those sampled along the EARS. At Nyamulagira, $CO_2/^{3}He$ is equal to 1.0×10^{10} (one measurement) and ranges from 2.2 to 2.3×10^{10} (two measurements) at Nyiragongo. These values are almost one order of magnitude higher than measured in Ol Doinyo Lengaï emissions representative of the SCLM beneath the Eastern Branch of the EARS (Fig. 5a). Considering the emission of natrocarbonatites at the Ol Doinyo Lengaï volcano and the hyperalkaline nature of the cogenetic nephelinitic melts (Fischer et al., 2009), such an increase of the $CO_2/^{3}He$ seems hardly reconcilable with a differential CO_2-He solubility effect in alkaline melts. The absence of significant $^{4}He/^{40}Ar^{*}$ increase does not sustain the effect of equilibrium degassing on the increase of $CO_2/^{3}He$ either (Burnard et al., 2004) (Fig. S-1). High $CO_2/^{3}He$ in gas emissions at Nyamulagira and Nyiragongo are rather ascribed to various extents of mixing with either (i) a hosted sediment-limestone crustal source (Darrah et al., 2013) or (ii) mantellic carbonates as observed in other continental rift systems (Frezzotti & Touret, 2014).

The absence of important change of $\delta^{13}C$ values at high $CO_2/^{3}He$ with respect to the SCLM (Fig. 5b) minimizes the likelihood of the influence of an interaction with crustal sediment or limestone as evidenced in regional hot springs (Tedesco et al., 2010). Once again, the presence of carbonate-bearing metasomes in the SCLM source derived from deeper fluids, as extensively documented along the Western Branch of the EARS (Rooney et al., 2020; Aiuppa et al., 2021), may provide a reasonable explanation to such a $CO_2/^{3}He$ increase at quite constant $\delta^{13}C$ (-1 to -8 ‰ for primary carbonatites; Harmer, 1999; Casola et al., 2020). This hypothesis is sustained by the chemistry of lavas emitted at Nyiragongo and Nyamulagira that points out limited contamination processes at crustal levels and rather emphasizes carbonate metasomatism in the mantle source beneath Nyiragongo (Chakrabarti et al., 2009; Pouclet et al., 2016; Aiuppa et al., 2021).

4.3. Potential sources of heterogeneities between gaseous emissions at Nyiragongo and Nyamulagira

If the composition of fumaroles at both Nyiragongo and Nyamulagira (12 km away from one another) share common features with respect to other volcanic emissions along the EARS, both

present distinct $\delta^{13}C$ signatures of CO_2 and $CO_2/^3He$ values (Fig. 3 and 4). We identified three potential scenarios that might account for such chemical variability.

In the first scenario ('1' on Fig. 5), a process of Rayleigh fractional condensation (about 50 %) of CO_2 during the ascent of the gas phase up to the surface (Mook et al., 1974) could account for (i) the lowest $CO_2/^3He$ and $\delta^{13}C$ values and (ii) the enrichment in less condensable gas species such a He, Ne, Ar (Table S-2) observed at Nyamulagira with respect to Nyiragongo. This process was extensively documented in peripheral "cold" dry CO_2-rich emission (so-called "mazukus") located on the edge of the Lake Kivu (Fig. 1; Tedesco et al., 2010). However, this process suggests a common source of magmatic fluids at both volcanoes (similar initial $CO_2/^3He$ and $\delta^{13}C$ of CO_2 before condensation) that hardly reconciliates the variations observed in the chemistry of "high temperature" volcanic gas plumes between both volcanoes (Fig. 2a; Bobrowski et al., 2017) and in the lava chemistry (Chakrabarti et al., 2009; Pouclet et al., 2016).

In the second scenario ('2' on Fig. 5), the composition of the fumaroles at Nyamulagira represents a mixing between fluids with $CO_2/^3He$ and $\delta^{13}C$ values similar to those measured in the fumaroles of Nyiragongo (80%) and fluids from a partially degassed mantle plume component as proposed in Afar (20%). The analysis of halogen elements in volcanic gas plumes at both Nyamulagira and Nyiragongo also suggests a greater affinity of the former with the volcanic gas plume at Erta Ale (Bobrowski et al., 2017). However, lava isotopic chemistry rather supports the opposite scenario: the (Sr-Nd-Pb) isotopic composition of lavas at Nyiragongo ranges intermediate between those at the Nyamulagira volcano and the Common ('C'-type) mantle plume component described in the Afar region (Chakrabarti et al., 2009; Rooney et al., 2020). In view of the contrast between the information provided by the chemical composition of the volcanic gas and those from the associated lava, this second scenario seems unlikely.

While we have ruled out a major involvement of a limestone or sedimentary source to explain the high $CO_2/^3He$ values measured in volcanic gas emitted at Nyiragongo and Nyamulagira, we cannot exclude that the inner variability observed in $\delta^{13}C$ values between both volcanoes may reflect the slight contribution of a recycled component. In this third scenario ('3' on Fig. 5), a small addition (<0.1 %) of recycled sediments could explain the more negative $\delta^{13}C$ values at Nyamulagira with respect to those at Nyiragongo. This recycled component may be either (i) intrinsic to the mantle source through the involvement of a recycled crustal material as suggested by the isotopic composition of lavas at Nyamulagira (Chakrabarti et al., 2009) or (ii) shallower, i.e., related to the interaction with metasediments at crustal level or organic matter close to the surface like observed in hot springs (Tedesco, 1995; Tedesco et al., 2020; Darrah et al., 2013). In both cases, the involvement of a biogenic and potentially hydrated component could provide one explanation to the (H_2O-CO_2-S_t) affinity of the volcanic gas plume of Nyamulagira with the range of composition defined by arc volcanism (Fig. 2a; Burton et al., 2000; Aiuppa et al., 2017).

We recognize that further work is required to better identify the origin of the heterogeneity in gaseous emissions between both volcanoes. Meanwhile, it is worth nothing that the last two scenarios required an initially lower $CO_2/^3He$ at Nyamulagira ($< 1.2 \times 10^{10}$; Fig. 5b) that agrees with a lesser extent of carbonate metasomatism in the mantle source beneath Nyamulagira. This is consistent with the chemical studies (Chakrabarti et al., 2009; Pouclet et al., 2016) that ascribe the composition of Nyamulagira and Nyiragongo lavas to a mantle source incorporating preferentially either a recycled crustal component or a carbonated component, respectively.

5 Conclusions

Fumaroles and volcanic gas plume sampling was conducted in February 2020 at the neighboring Nyamulagira and Nyiragongo volcanoes in the Virunga Volcanic Province along the Western Branch of the EARS. The isotope chemistry of the fumaroles and the composition of the volcanic gas plume discard a major contribution of a high $^{3}He/^{4}He$ mantle plume component in the genesis of volcanic fluids beneath the area. $CO_2/^{3}He$ values measured at both volcanoes are higher than values reported for other persistently active volcanoes along the EARS suggesting carbonate metasomatism in the Sub-Continental Lithospheric Mantle (SCLM), especially beneath Nyiragongo. This result is consistent with the chemical investigation of lavas performed in the area (Chakrabarti et al., 2009; Pouclet et al., 2021) and more globally with the presence of numerous mantle metasomes beneath the Western Branch of the EARS. Heterogeneities between gaseous emissions at Nyiragongo and Nyamulagira mainly relate to the composition of the volcanic gas plume and the $\delta^{13}C$ of the CO_2 in fumaroles. We stress that such variability could reflect the influence of a biogenic and/or more hydrated component expressed in volcanic fluids at Nyamulagira.

Acknowledgments, Samples, and Data

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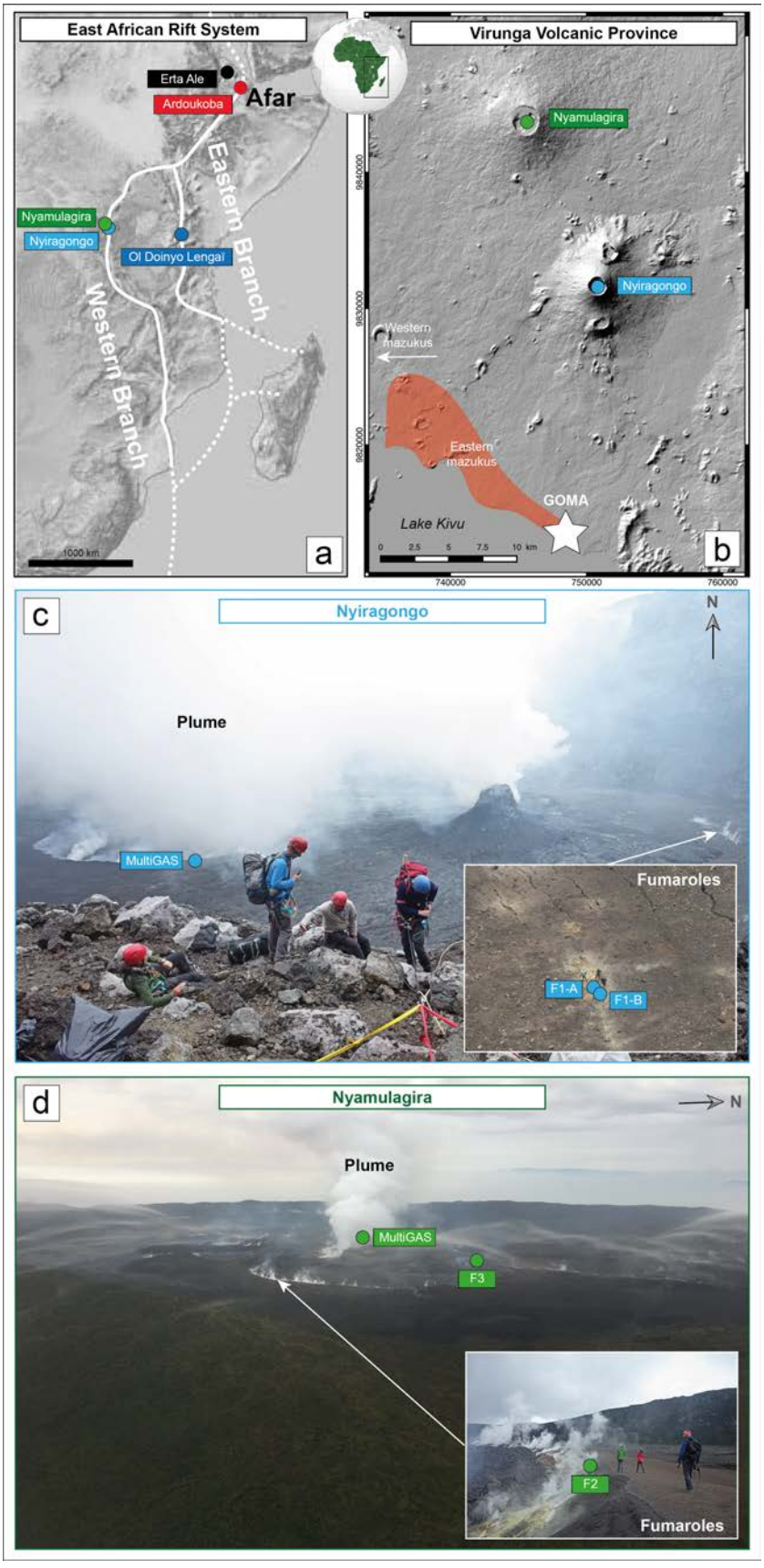

East African Rift System
Erta Ale
Ardoukoba
Afar
Eastern Branch
Western Branch
Nyamulagira
Nyiragongo
Ol Doinyo Lengai
1000 km
a
Virunga Volcanic Province
Nyamulagira
Nyiragongo
Western mazukus
Eastern mazukus
GOMA
Lake Kivu
0 2.5 5 7.5 10 km
9840000
9830000
9820000
740000
750000
760000
b
c
Nyiragongo
N
Plume
MultiGAS
Fumaroles
F1-A
F1-B
d
Nyamulagira
N
Plume
MultiGAS
F3
F2
Fumaroles

565

Fig. 1 Location of volcanoes currently in eruption (plus the 1978 Ardoukoba eruption) (a) along the EARS and (b) in the Virunga Volcanic Province. The area of the cold dry CO_2-rich emission so-called "mazukus" are indicated in red (Tedesco et al., 2010). Volcanic gas plume and fumaroles sampling sites at (c) Nyiragongo and (d) Nyamulagira.

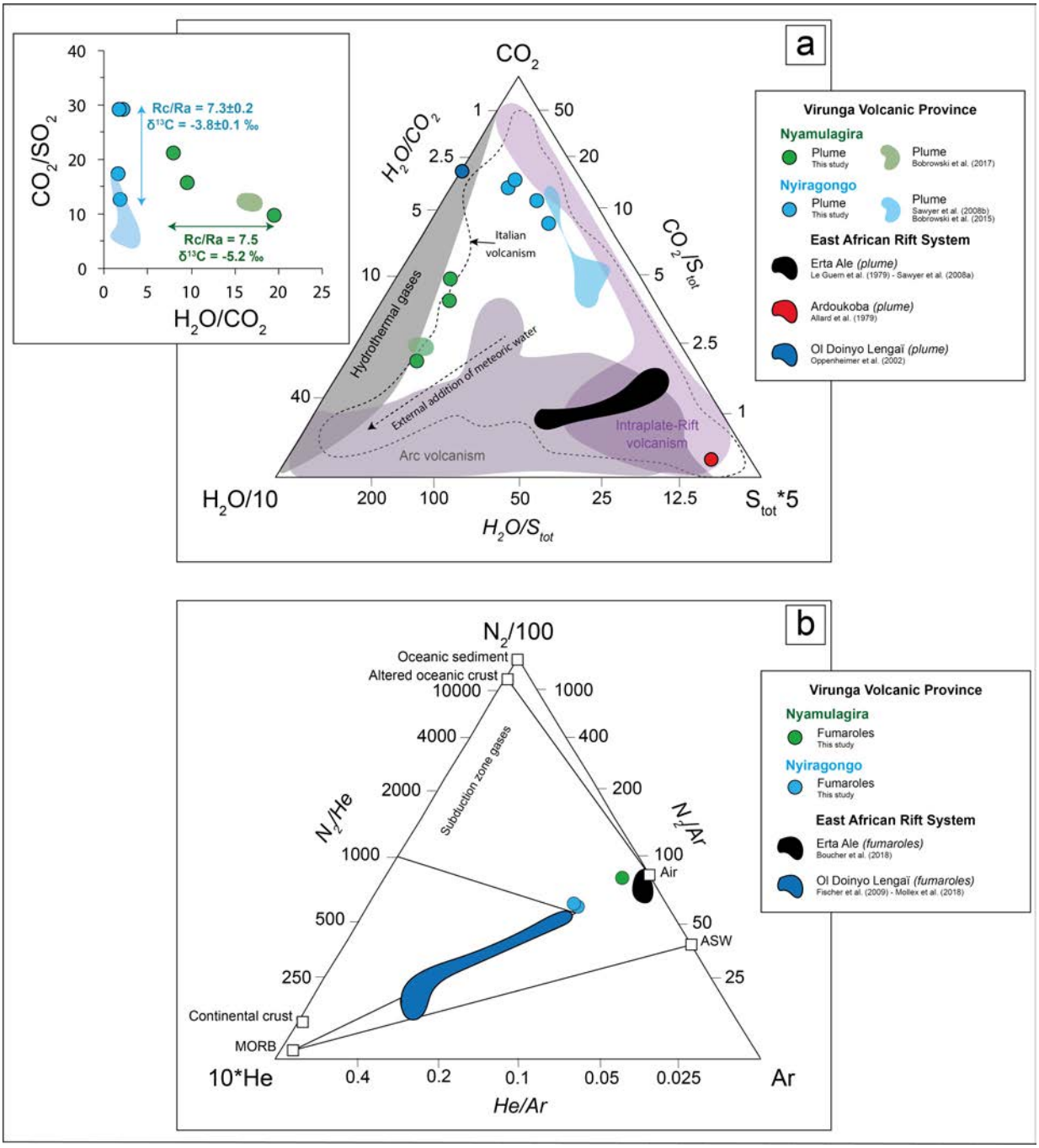
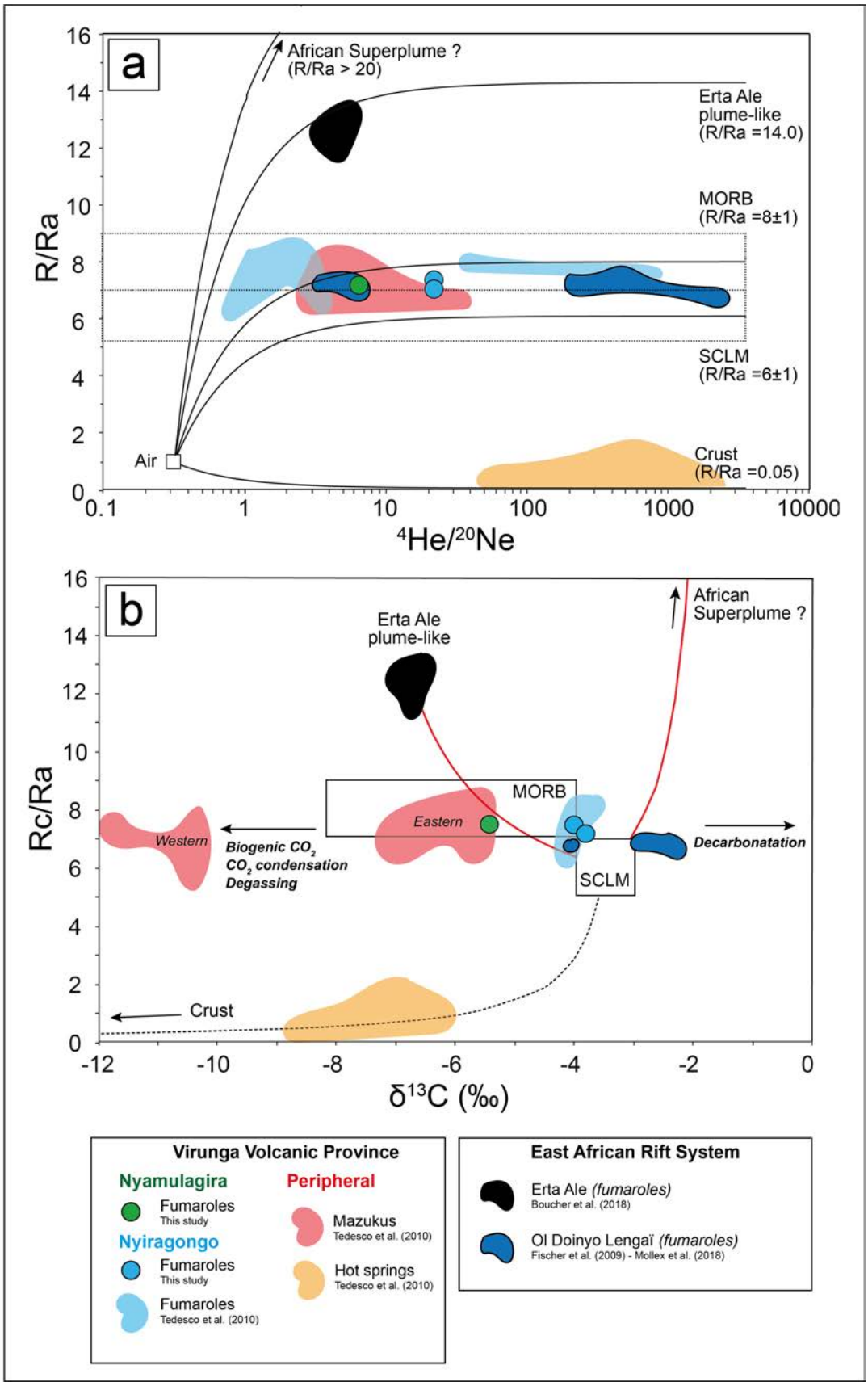


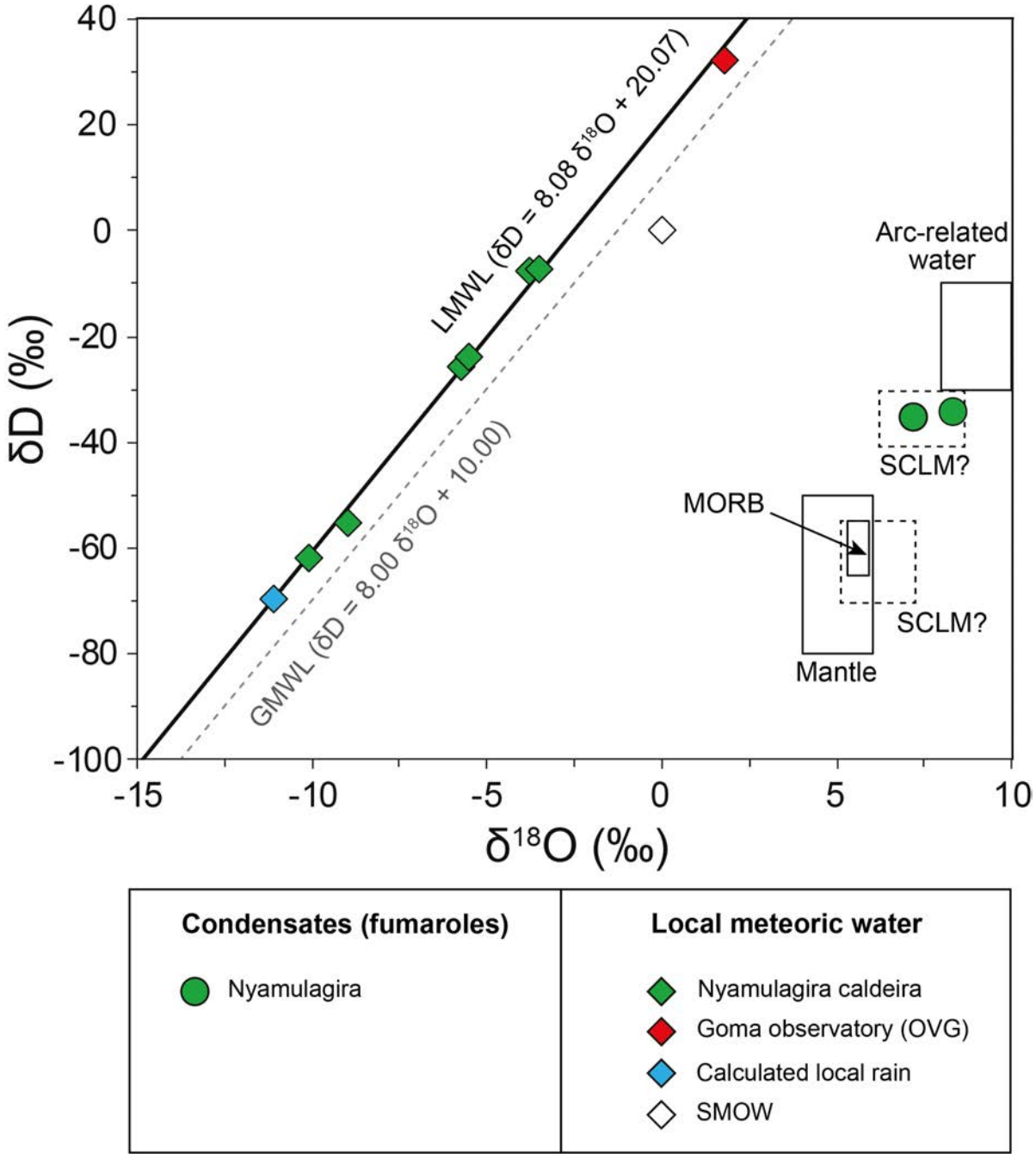
Fig. 2 (a) MultiGAS measurements performed in the volcanic gas plume of Nyiragongo and Nyamulagira during the 2020 field mission. Rc/Ra and $\delta^{13}C$ values from fumaroles (inlay). Data for volcanism gas plume and high temperature (> 500°C) fumaroles (arc volcanism, intraplate-rift volcanism, Italian volcanism) and for hydrothermal gases have been compiled from Aiuppa et al.

(2015, 2016), Lages et al. (2020) and Henley and Fischer (2021). (b) N_2-He-Ar ternary diagram of fumaroles composition along the EARS.


a
African Superplume ?
(R/Ra > 20)
Erta Ale
plume-like
(R/Ra =14.0)
MORB
(R/Ra =8±1)
SCLM
(R/Ra =6±1)
Crust
(R/Ra =0.05)
Air
R/Ra
$^4He/^{20}Ne$
b
Erta Ale
plume-like
African
Superplume ?
MORB
Eastern
Western
Biogenic CO_2
CO_2 condensation
Degassing
Decarbonatation
SCLM
Crust
Rc/Ra
$\delta^{13}C$ (‰)
Virunga Volcanic Province
Nyamulagira
Fumaroles
This study
Nyiragongo
Fumaroles
This study
Fumaroles
Tedesco et al. (2010)
Peripheral
Mazukus
Tedesco et al. (2010)
Hot springs
Tedesco et al. (2010)
East African Rift System
Erta Ale (fumaroles)
Boucher et al. (2018)
Ol Doinyo Lengaï (fumaroles)
Fischer et al. (2009) - Mollex et al. (2018)

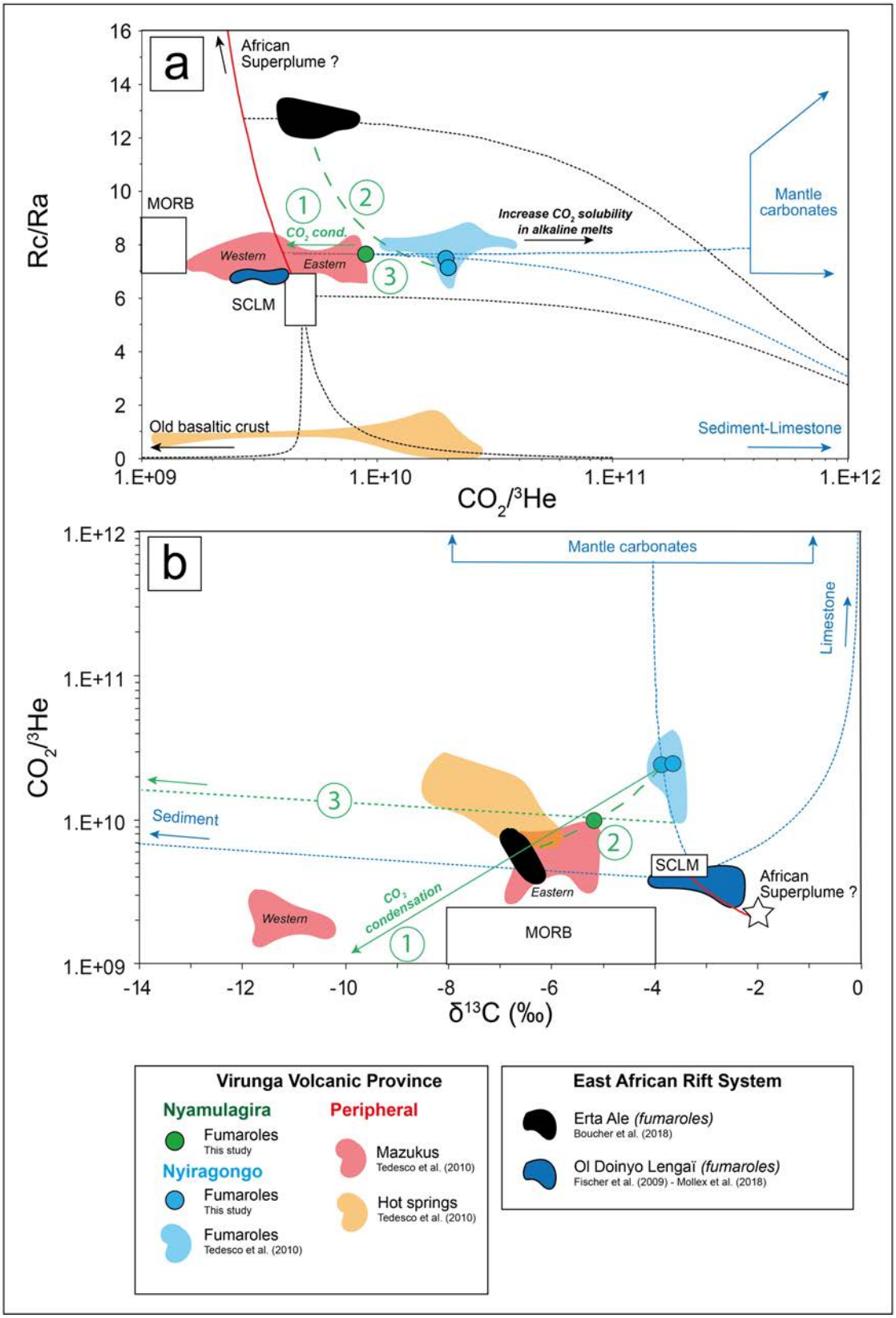
579

Fig. 3 (a) $^{4}He/^{20}Ne$ vs. R/Ra. Black lines for mixing between the air and terrestrial end-members. (b) $\delta^{13}C$ vs. Rc/Ra. Red continuous lines for mixing between potential mantle plume-like components and the SCLM. Black dashed lines for mixing between SCLM and crustal components as testified by the chemical composition of the gas emissions from hot springs in the Virunga Volcanic Province (Tedesco et al., 2010).



585
586
587

588 **Fig. 4** Isotopic composition ($\delta^{18}O$ and $\delta^{2}D$ of H_2O) of condensates from fumarole F3 at
589 Nyamulagira and local rainwater samples collected beneath the volcanic gas plume at Nyamulagira
590 and at the Observatoire Volcanologique de Goma. The Local Meteoric Water Line is calculated
591 from the collected rainwater samples (see Methods for details). Inferred range of isotopic values
592 for the SCLM (dashed rectangles) from Taran and Zelenski (2015).
593


a
African Superplume ?
MORB
SCLM
Western
Eastern
CO2 cond.
Increase CO2 solubility in alkaline melts
Mantle carbonates
Old basaltic crust
Sediment-Limestone
Rc/Ra
CO2/3He
b
Mantle carbonates
Limestone
Sediment
CO2 condensation
SCLM
African Superplume ?
Eastern
Western
MORB
CO2/3He
δ13C (‰)
Virunga Volcanic Province
Nyamulagira
Fumaroles
This study
Nyiragongo
Fumaroles
This study
Fumaroles
Tedesco et al. (2010)
Peripheral
Mazukus
Tedesco et al. (2010)
Hot springs
Tedesco et al. (2010)
East African Rift System
Erta Ale (fumaroles)
Boucher et al. (2018)
Ol Doinyo Lengaï (fumaroles)
Fischer et al. (2009) - Mollex et al. (2018)

595 **Fig. 5** (a) $CO_2/^3He$ vs. Rc/Ra and (b) $\delta^{13}C$ vs. $CO_2/^3He$. Continuous red line for mixing between
596 the "African Superplume" component and the SCLM. Black and blue dotted lines for mixing with
597 distinct crustal components or mantle carbonates (blue dotted lines are those discussed in the text
598 about the geochemical variability of gaseous emissions in the Virunga Volcanic Province with
599 respect to the EARS). Green continuous, dotted and dashed lines relate to scenarios 1-2-3
600 discussed in the text and accounting for the chemical variability of gaseous emissions between
601 Nyamulagira and Nyiragongo. CO_2 condensation process from Mook et al. (1974) computed with
602 a temperature of 80°C similar to that measured in the fumaroles at Nyamulagira.