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

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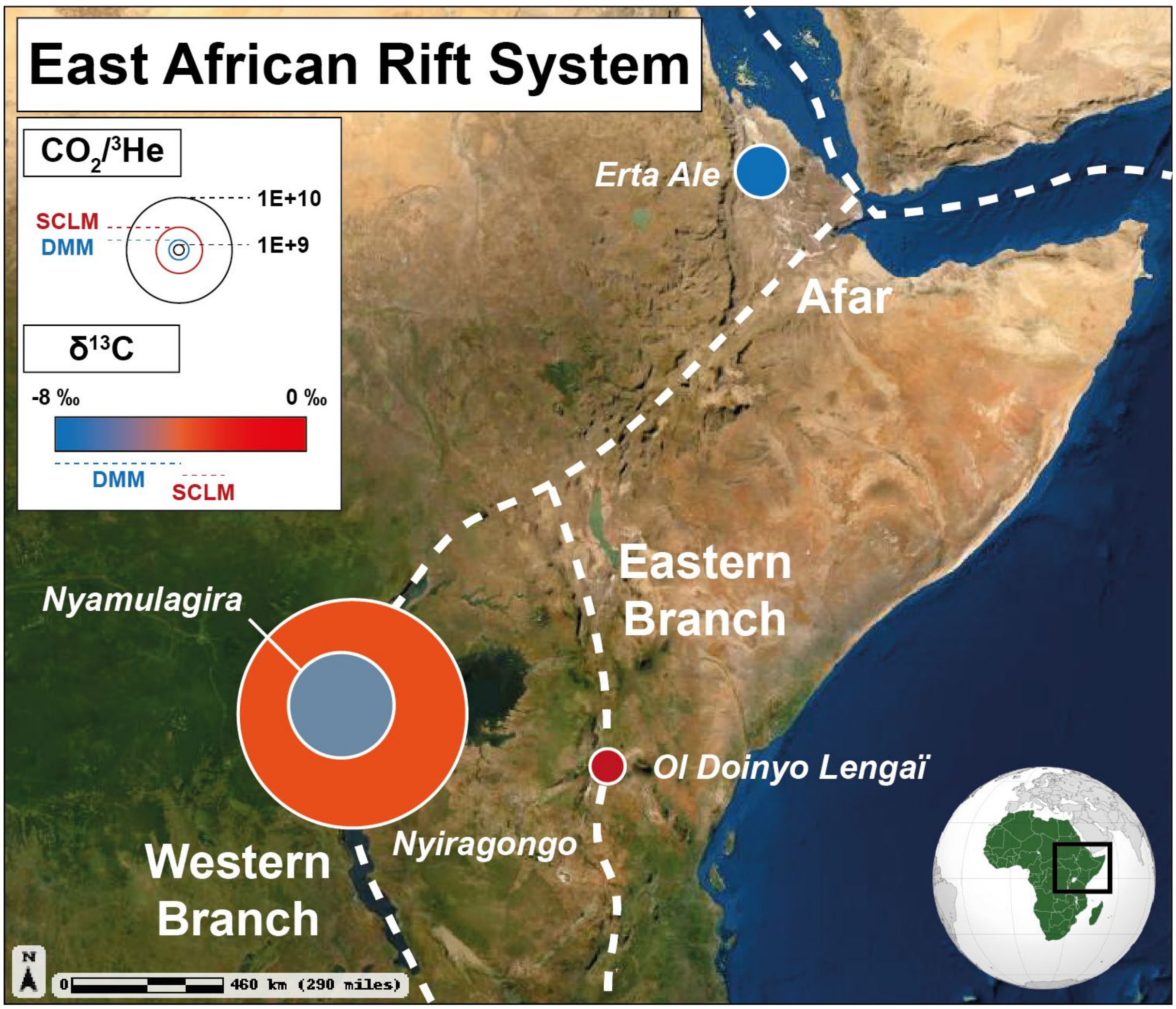
Highlights:

- Origin of volcanic CO_2 emissions along the East African Rift System
- Role of the Sub-Continental Lithospheric Mantle in the genesis of magmatic fluids beneath the Virunga Volcanic Province
- Carbonate metasomatism of the mantle source

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 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 the Sub-Continental Lithospheric Mantle (SCLM) and deeper fluids. At Nyiragongo and Nyamulagira, our study suggests that volcanic gas emissions preserve the fingerprint of the SCLM. High $CO_2/^3He$ in fumaroles of both volcanoes is thought to reflect carbonate metasomatism in the mantle source. As inferred by previous results obtained on the lava chemistry, this carbonate metasomatism would be more pronounced beneath Nyiragongo.

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, also the role of continental rifting on the global carbon budget and climate dynamics has 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 peculiarity of the EARS concerning the cycling of volatiles elements. However, the origin of such 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 distinct shallow mantle plumes upwelling (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. "African Superplume") and (2) the Sub-Continental Lithospheric Mantle 'SCLM'.

A field survey in the Virunga Volcanic Province (Democratic Republic of Congo) in 2020 allowed gas collection from volcanic plumes and fumaroles 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 (see Results in Supplementary Information; Fig. 2). By compiling previous chemical data obtained from fumaroles and volcanic plumes 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 gaseous 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 and further two 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 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). 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). Glass samplers were used on line with a 50 cm stainless-steel tube and Dewar glass tubes (Vaselli et al., 2006). Collected gas samples were then analyzed 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, $\delta^{18}O$ and $\delta^{2}D$ of H_2O) (Table S-2). The analytical procedure and correction for air-contamination of noble gases are the same as the ones described in Boudoire et al. (2020). In the figures (Fig. 2, 3, 4, 5), the analytical uncertainty on laboratory measurements is less than the size of the symbol.

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 fumaroles (Table S-2) and rainwaters (Table S-3) were analyzed at the Osservatorio Vesuviano (INGV) (see Brombach et al. (2003) for details about the analytical procedure). 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 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), Darrah et al. (2013), Bobrowski et al. (2017), Boucher et al. (2018) and Mollex et al. (2018). The composition of the end-members (DMM, African Superplume, SCLM, Continental Crust, Oceanic Crust, Limestone, Sediments, Mantle carbonates, Air and ASW) used to define the mixing curves are defined from Sheppard & Epstein (1970), Harmer (1999), Gautheron & Moreira (2002), Pik et al. (2006), Zelenski & Taran (2011), Barry et al. (2013), Clog et al., (2013), Hallis et al. (2015) and Taran & Zelenski (2015), Casola et al. (2020).

3 Results

MultiGAS measurements in volcanic 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 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 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 point out a CO_2/SO_2 range at Nyamulagira (9.7-21.1) overlapped by Nyiragongo's one (5.0-29.1) while the H_2O/CO_2 range 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 set in fumarole (F2) at Nyamulagira with N_2/He = 6814 and N_2/Ar = 93. These values fall very well in what is 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; 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) and slightly higher than measured at Ol Doinyo Lengaï (0.45-0.76; Fischer et al., 2009).

Carbon isotopes evidence the largest variability between the fumaroles of both volcanoes (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 (Fig. 4; Taran & Zelenski, 2015).

4. Discussion

4.1. Contribution of the SCLM 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. "African Superplume") and a SCLM (Halldorsson et al., 2014; Mollex et al., 2018; O'Connor et al., 2019) component. In this frame, measurements obtained in the Afar (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 representative of the predominant contribution of the SCLM in the genesis of magmatic fluids (Mollex et al., 2018).

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). Actually, $\delta^{13}C$ values of CO_2 at Nyiragongo (Fig. 3b) and $\delta^{18}O$ and δD measurements of H_2O at Nyamulagira are rather similar to what expected from the contribution of the SCLM in the genesis of magmatic fluids (Fig. 4), as proposed at the Ol Doinyo Lengaï on the other branch of the EARS (Mollex et al., 2018). The composition of the volcanic gas plumes (H_2O – CO_2 – S_t; Fig. 2a) at both Nyamulagira and Nyiragongo is also strongly different than that measured during the 1978 Ardoukoba eruption fed by E-MORB magma (Vigier et al., 1999).

Our results match with previous conclusions from petrological investigations along the Western Branch of the EARS that discard a predominant contribution of a DMM source in the genesis of magmatic fluids there (Rosenthal et al., 2009; Rooney et al., 2020). Conversely, partial involvement of deeper mantellic fluids may provide a reasonable explanation to the slight enrichment in primordial helium (^3He) 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). Mantle reservoirs at the origin of such an enrichement in ^3He in the SCLM may involve indistinguishably: an undegassed archetypal mantle plume like the African Superplume (Darrah et al., 2013), a partially degassed mantle plume component 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 is required to distinguish the influence of the components beneath the province.

4.2. Carbon enrichment tracked by gaseous emissions

The composition of the fumaroles in the Virunga Volcanic Province strongly differs from those sampled along the EARS when looking at $CO_2/^3He$ values. At Nyamulagira, $CO_2/^3He = 1.0 \times 10^{10}$ and ranges from 2.2 to 2.3 x 10^{10} 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 $CO_2/^3He$ seems hardly reconcilable with a differential CO_2-He solubility effect in alkaline melts. The absence of significative $^4He/^{40}Ar^*$ increase neither sustains the effect of equilibrium degassing in the increase of $CO_2/^3He$ (Burnard et al., 2004) as suggested in some gaseous emissions at Dallol (cf. Gr. I on Fig. S-1; Darrah et al., 2013). High $CO_2/^3He$ in gas emissions at Nyamulagira and Nyiragongo are rather ascribed to various extent 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 $CO_2/^3He$ with respect to the SCLM (Fig. 5b) minimizes the likelihood of (i) the influence of an interaction with crustal sediment or limestone as proposed at Dallol (Darrah et al., 2013) or evidenced in regional hot springs (Tedesco et al., 2010). Once again, (ii) 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 $CO_2/^3He$ 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 far away only) share common features with respect to other volcanic emissions along the EARS, both present distinct

$\delta^{13}C$ signature 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 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 represent a mixing between mantle fluids similar to those emitted at Nyiragongo (80%) and fluids from a partially degassed mantle component as proposed in the Afar (20%). The analysis of halogen elements in volcanic plumes at both Nyamulagira and Nyiragongo also suggests a better affinity of the former with the volcanic 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 the 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 at Dallol (e.g., transition from Gr. I to Gr. II; 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 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 x 10^{10}; Fig. 5b) that agrees with a lesser extent of carbonate metasomatism in the mantle source beneath Nyamulagira following the above discussion (Chakrabarti et al., 2009; Pouclet et al., 2016) where both Nyamulagira and Nyiragongo lavas are ascribed to a mantle source incorporating preferentially either a recycled crustal component or a carbonated component, respectively.

5 Conclusions

Fumaroles and volcanic 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 plume suggests the contribution of the Sub-Continental Lithospheric Mantle (SCLM) in the genesis of volcanic fluids beneath the area. $CO_2/^3He$ measured at both volcanoes is higher than values reported for other persistently active volcanoes along the EARS and suggests carbonate metasomatism in the mantle source, especially beneath Nyiragongo. This result is consistent with the chemical investigation of lavas performed in the area 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 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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References

Aiuppa A., Federico C., Giudice G., Gurrieri S., Liuzzo M., Shinohara H., Favara R. & Valenza M. (2006). Rates of carbon dioxide plume degassing from Mount Etna volcano. *J. Geophys. Res.*, 111, B09207, doi:10.1029/2006JB004307.

Aiuppa, A., Fischer, T. P., Plank, T., Robidoux, P., & Di Napoli, R. (2017). Along-arc, inter-arc and arc-to-arc variations in volcanic gas CO2/ST ratios reveal dual source of carbon in arc volcanism. *Earth-Science Reviews*, 168, 24-47.

Allard, P., Tazieff, H., & Dajlevic, D. (1979). Observations of seafloor spreading in Afar during the November 1978 fissure eruption. *Nature*, 279(5708), 30-33.

Barry, P. H., Hilton, D. R., Fischer, T. P., De Moor, J. M., Mangasini, F., & Ramirez, C. (2013). Helium and carbon isotope systematics of cold "mazuku" CO2 vents and hydrothermal gases and fluids from Rungwe Volcanic Province, southern Tanzania. *Chemical Geology*, 339, 141-156.

Bobrowski, N., Giuffrida, G. B., Yalire, M., Lübcke, P., Arellano, S., Balagizi, C., Calabrese, S., Galle, B., & Tedesco, D. (2017). Multi-component gas emission measurements of the active lava lake of Nyiragongo, DR Congo. *Journal of African Earth Sciences*, 134, 856-865.

Boucher, C., Lan, T., Marty, B., Burnard, P. G., Fischer, T. P., Ayalew, D., Mabry, J., Maarten de Moor, J., Zelenski, M.E., & Zimmermann, L. (2018). Atmospheric helium isotope composition as a tracer of volcanic emissions: A case study of Erta Ale volcano, Ethiopia. *Chemical Geology*, 480, 3-11.

Boudoire, G., Rizzo, A. L., Arienzo, I., & Di Muro, A. (2020). Paroxysmal eruptions tracked by variations of helium isotopes: inferences from Piton de la Fournaise (La Réunion island). *Scientific reports*, 10(1), 1-16.

Bowen, G. J., & Wilkinson, B. (2002). Spatial distribution of δ18O in meteoric precipitation. *Geology*, 30(4), 315-318.

Bräuer, K., Geissler, W. H., Kämpf, H., Niedermannn, S., & Rman, N. (2016). Helium and carbon isotope signatures of gas exhalations in the westernmost part of the Pannonian Basin (SE Austria/NE Slovenia): Evidence for active lithospheric mantle degassing. *Chemical Geology*, 422, 60-70.

Brombach, T., Caliro, S., Chiodini, G., Fiebig, J., Hunziker, J. C., & Raco, B. (2003). Geochemical evidence for mixing of magmatic fluids with seawater, Nisyros hydrothermal system, Greece. *Bulletin of Volcanology*, 65(7), 505-516.

Burgi, P. Y., Boudoire, G., Rufino, F., Karume, K., & Tedesco, D. (2020). Recent activity of Nyiragongo (Democratic Republic of Congo): New insights from field observations and numerical modeling. *Geophysical Research Letters*, 47(17), e2020GL088484.

Burnard, P., Graham, D., & Farley, K. (2004). Fractionation of noble gases (He, Ar) during MORB mantle melting: a case study on the Southeast Indian Ridge. *Earth and Planetary Science Letters*, 227(3-4), 457-472.

Burton, M. R., Oppenheimer, C., Horrocks, L. A., & Francis, P. W. (2000). Remote sensing of CO2 and H2O emission rates from Masaya volcano, Nicaragua. *Geology*, 28(10), 915-918.

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). *Geochimica et Cosmochimica Acta*, 75(23), 7401-7425.

Casola, V., France, L., Galy, A., Bouden, N., & Villeneuve, J. (2020). No evidence for carbon enrichment in the mantle source of carbonatites in eastern Africa. Geology, 48(10), 971-975.

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. *Chemical Geology*, 259(3-4), 273-289.

Clog, M., Aubaud, C., Cartigny, P., & Dosso, L. (2013). The hydrogen isotopic composition and water content of southern Pacific MORB: A reassessment of the D/H ratio of the depleted mantle reservoir. *Earth and Planetary Science Letters*, 381, 156-165.

Darrah, T. H., Tedesco, D., Tassi, F., Vaselli, O., Cuoco, E., & Poreda, R. J. (2013). Gas chemistry of the Dallol region of the Danakil Depression in the Afar region of the northern-most East African Rift. *Chemical Geology*, 339, 16-29.

Fischer, T. P., Burnard, P., Marty, B., Hilton, D. R., Füri, E., Palhol, F., Sharp, Z.D., & Mangasini, F. (2009). Upper-mantle volatile chemistry at Oldoinyo Lengai volcano and the origin of carbonatites. *Nature*, 459(7243), 77-80.

Frezzotti, M. L., & Touret, J. L. (2014). CO2, carbonate-rich melts, and brines in the mantle. *Geoscience Frontiers*, 5(5), 697-710.

Gautheron, C., & Moreira, M. (2002). Helium signature of the subcontinental lithospheric mantle. *Earth and Planetary Science Letters*, 199(1-2), 39-47.

Gerlach, T. M. (1982). Interpretation of volcanic gas data from tholeiitic and alkaline mafic lavas. *Bulletin Volcanologique*, 45(3), 235-244.

Halldórsson, S. A., Hilton, D. R., Scarsi, P., Abebe, T., & Hopp, J. (2014). A common mantle plume source beneath the entire East African Rift System revealed by coupled helium-neon systematics. *Geophysical Research Letters*, 41(7), 2304-2311.

Hallis, L. J., Huss, G. R., Nagashima, K., Taylor, G. J., Halldórsson, S. A., Hilton, D. R., Motti, M.J., & Meech, K. J. (2015). Evidence for primordial water in Earth's deep mantle. *Science*, 350(6262), 795-797.

Harmer, R. E. (1999). The petrogenetic association of carbonatite and alkaline magmatism: constraints from the Spitskop Complex, South Africa. *Journal of Petrology*, 40(4), 525-548.

Liuzzo, M., Gurrieri, S., Giudice, G., & Giuffrida, G. (2013). Ten years of soil CO2 continuous monitoring on Mt. Etna: Exploring the relationship between processes of soil degassing and volcanic activity. *Geochemistry, Geophysics, Geosystems*, 14(8), 2886-2899.

Mollex, G., Füri, E., Burnard, P., Zimmermann, L., Chazot, G., Kazimoto, E. O., Marty, B., & France, L. (2018). Tracing helium isotope compositions from mantle source to fumaroles at Oldoinyo Lengai volcano, Tanzania. *Chemical Geology*, 480, 66-74.

Mook, W. G., Bommerson, J. C., & Staverman, W. H. (1974). Carbon isotope fractionation between dissolved bicarbonate and gaseous carbon dioxide. *Earth and Planetary Science Letters*, 22(2), 169-176.

O'Connor, J. M., Jokat, W., Regelous, M., Kuiper, K. F., Miggins, D. P., & Koppers, A. A. (2019). Superplume mantle tracked isotopically the length of Africa from the Indian Ocean to the Red Sea. *Nature communications*, 10(1), 1-13.

Oppenheimer, C., Burton, M. R., Durieux, J., & Pyle, D. M. (2002). Open-path Fourier transform spectroscopy of gas emissions from Oldoinyo Lengai volcano, Tanzania. *Optics and lasers in engineering*, 37(2-3), 203-214.

Pik, R., Marty, B., & Hilton, D. R. (2006). How many mantle plumes in Africa? The geochemical point of view. *Chemical Geology*, 226(3-4), 100-114.

Pouclet, A., Bellon, H., & Bram, K. (2016). The Cenozoic volcanism in the Kivu rift: Assessment of the tectonic setting, geochemistry, and geochronology of the volcanic activity in the South-Kivu and Virunga regions. *Journal of African Earth Sciences*, 121, 219-246.

Rizzo, A. L., Pelorosso, B., Coltorti, M., Ntaflos, T., Bonadiman, C., Matusiak-Małek, M., Italiano, F., & Bergonzoni, G. (2018). Geochemistry of noble gases and CO2 in fluid inclusions from lithospheric mantle beneath Wilcza Góra (Lower Silesia, southwest Poland). *Frontiers in Earth Science*, 6, 215.

Rooney, T. O. (2020). The Cenozoic magmatism of East Africa: part V–magma sources and processes in the East African Rift. *Lithos*, 360, 105296.

Rosenthal, A., Foley, S. F., Pearson, D. G., Nowell, G. M., & Tappe, S. (2009). Petrogenesis of strongly alkaline primitive volcanic rocks at the propagating tip of the western branch of the East African Rift. *Earth and Planetary Science Letters*, 284(1-2), 236-248.

Sano, Y, & Marty, B. (1995). Origin of carbon in fumarolic gas from island ars. *Chemical Geology*, 119, 265-274.

Sawyer, G. M., Carn, S. A., Tsanev, V. I., Oppenheimer, C., & Burton, M. (2008a). Investigation into magma degassing at Nyiragongo volcano, Democratic Republic of the Congo. *Geochemistry, Geophysics, Geosystems*, 9(2).

Sawyer, G. M., Oppenheimer, C., Tsanev, V. I., & Yirgu, G. (2008b). Magmatic degassing at Erta'Ale volcano, Ethiopia. *Journal of Volcanology and Geothermal Research*, 178(4), 837-846.

Sheppard, S. M., & Epstein, S. (1970). D/H and18O/16O ratios of minerals of possible mantle or lower crustal origin. *Earth and Planetary Science Letters*, 9(3), 232-239.

Taran, Y., & Zelenski, M. (2015). Systematics of water isotopic composition and chlorine content in arc-volcanic gases. *Geological Society, London, Special Publications*, 410(1), 237-262.

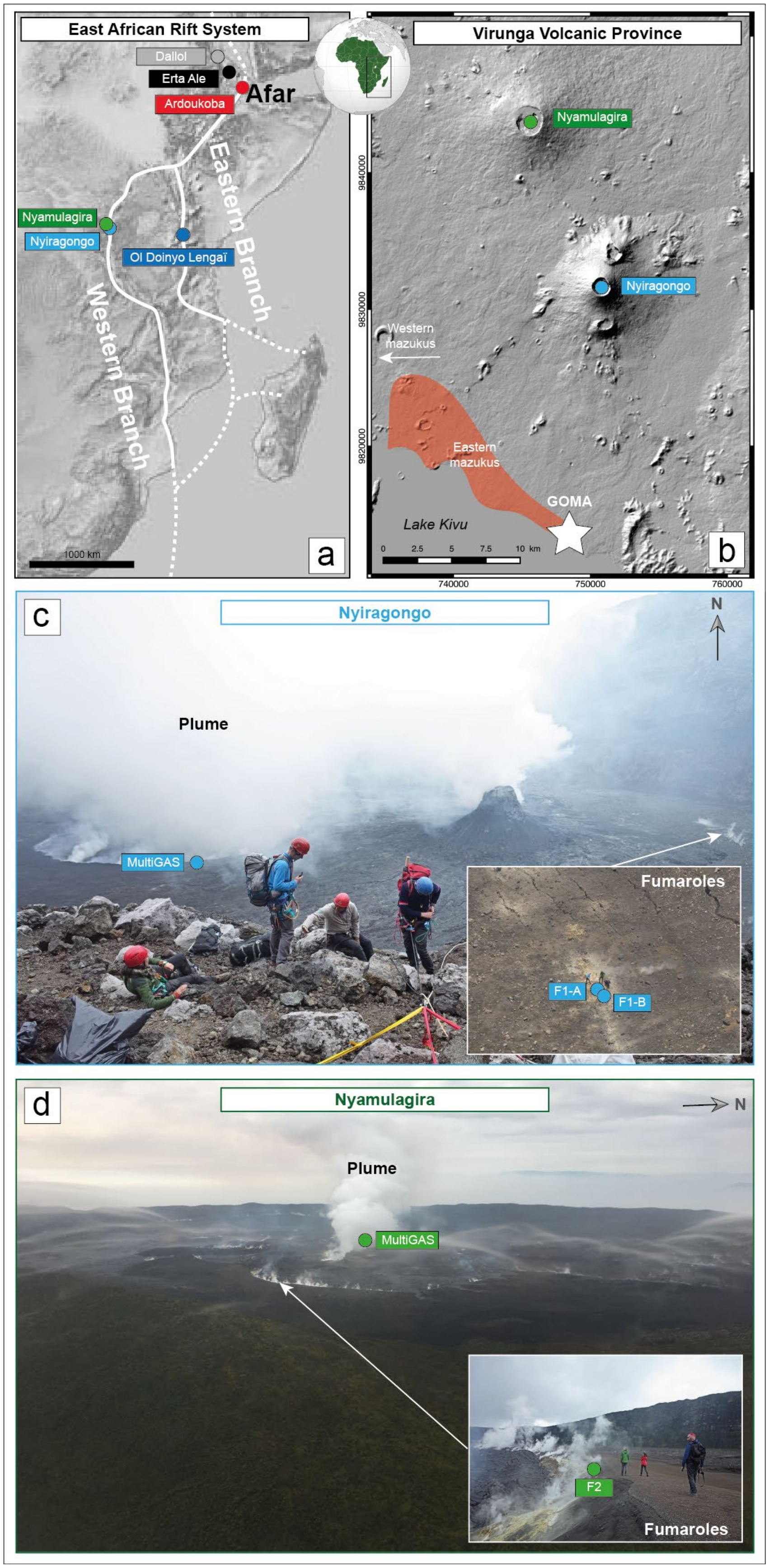
Tedesco, D., Tassi, F., Vaselli, O., Poreda, R. J., Darrah, T., Cuoco, E., & Yalire, M. M. (2010). Gas isotopic signatures (He, C, and Ar) in the Lake Kivu region (western branch of the East African rift system): Geodynamic and volcanological implications. *Journal of Geophysical Research: Solid Earth*, 115(B1).

Vaselli, O., Tassi, F., Montegrossi, G., Capaccioni, B., & Giannini, L. (2006). Sampling and analysis of volcanic gases. *Acta Vulcanologica*, 18(1/2), 67.

Vigier, N., Bourdon, B., Joron, J. L., & Allegre, C. J. (1999). U-decay series and trace element systematics in the 1978 eruption of Ardoukoba, Asal rift: timescale of magma crystallization. *Earth and Planetary Science Letters*, 174(1-2), 81-98.

Wong, K., Mason, E., Brune, S., East, M., Edmonds, M., & Zahirovic, S. (2019). Deep carbon cycling over the past 200 million years: a review of fluxes in different tectonic settings. *Frontiers in Earth Science,* 7, 1-22.

Zelenski, M., & Taran, Y. (2011). Geochemistry of volcanic and hydrothermal gases of Mutnovsky volcano, Kamchatka: evidence for mantle, slab and atmosphere contributions to fluids of a typical arc volcano. *Bulletin of Volcanology*, 73(4), 373-394.


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

459

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 plume and fumaroles sampling sites at (c) Nyiragongo and (d) Nyamulagira.

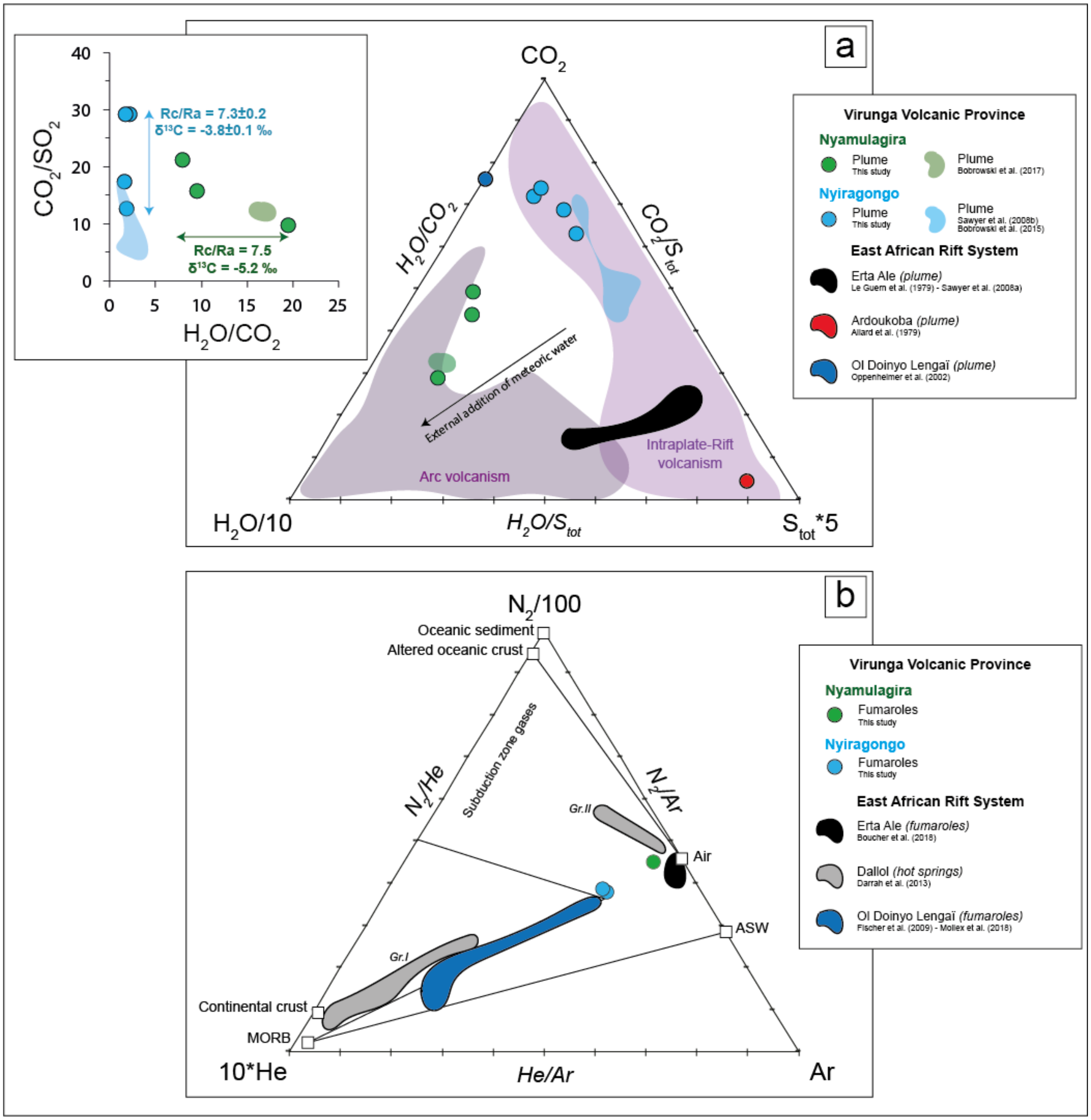


Fig. 2 (a) MultiGAS measurements performed in the volcanic plume of Nyiragongo and Nyamulagira during the 2020 field mission. Rc/Ra and $\delta^{13}C$ values from fumaroles (inlay). (b) N_2-He-Ar ternary diagram of fumaroles composition along the EARS. Gr.I and Gr.II are the two distinct chemical groups of gas emissions identified at Dallol (Darrah et al., 2013).

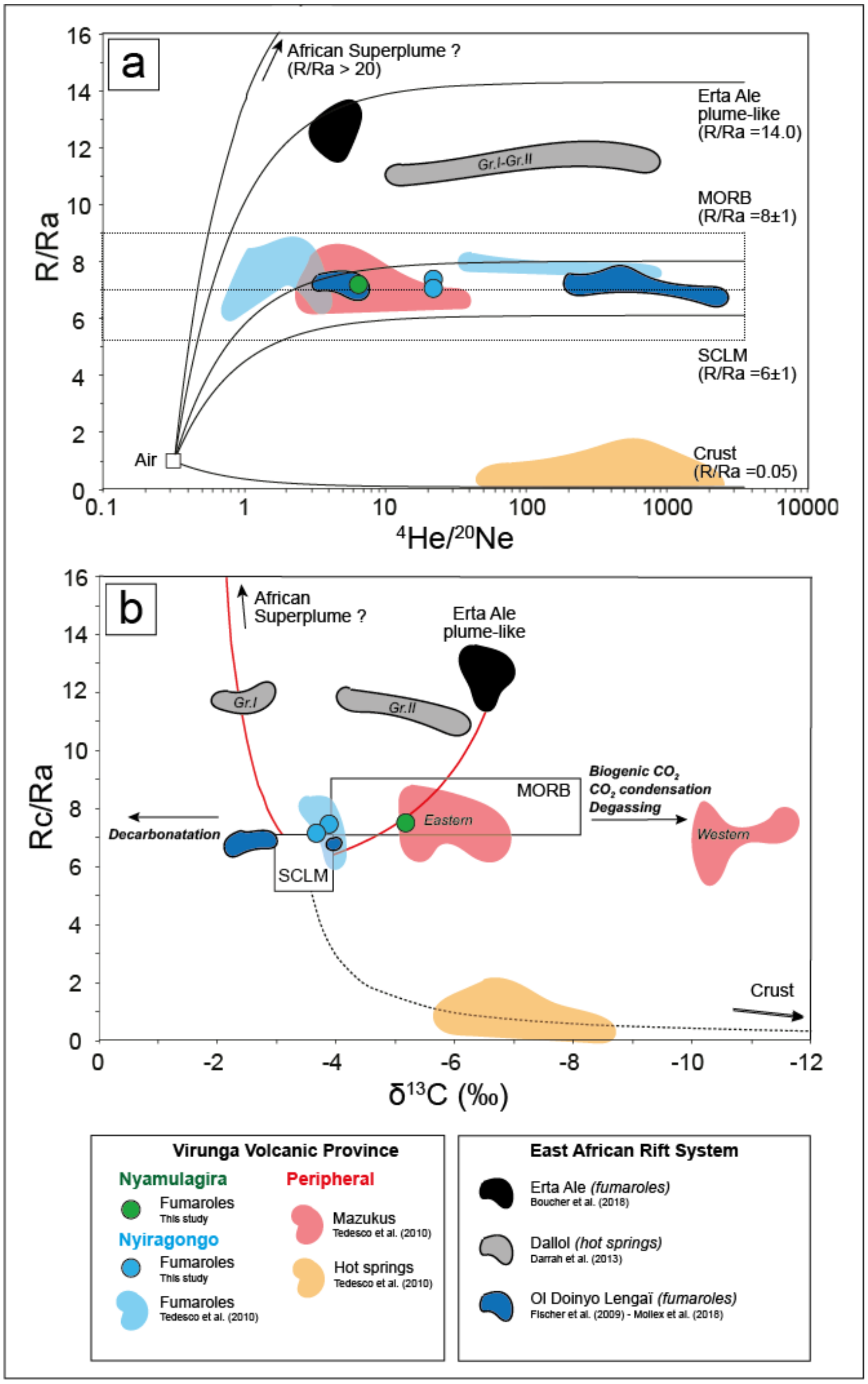


Fig. 3 (a) $^{4}He/^{20}Ne$ vs. R/Ra. Black lines for mixing between the air and terrestrial end-members. (b) $\delta^{13}C$ vs. Rc/Ra. Red continuous lines for mixing between potential mantle plume-like components and the SCLM. Black dashed lines for mixing between SCLM and crustal components as testified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

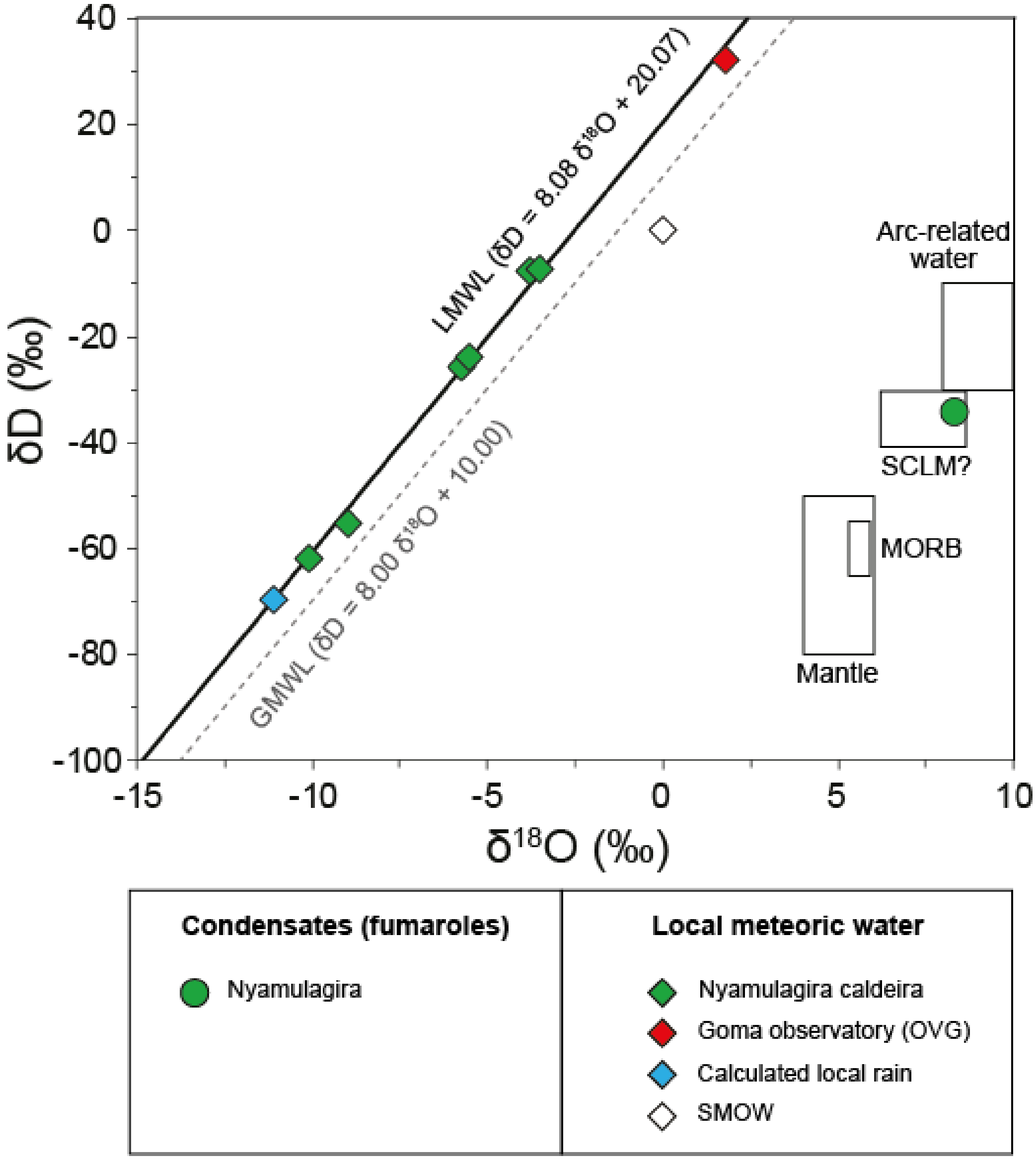


Fig. 4 Isotopic composition ($\delta^{18}O$ and $\delta^{2}D$ of H_2O) of condensates from fumaroles at Nyamulagira and local rainwater samples collected beneath the volcanic plume at Nyamulagira and at the Observatoire Volcanologique de Goma. The Local Meteoric Water Line is calculated from the collected rainwater samples (see Methods for details).

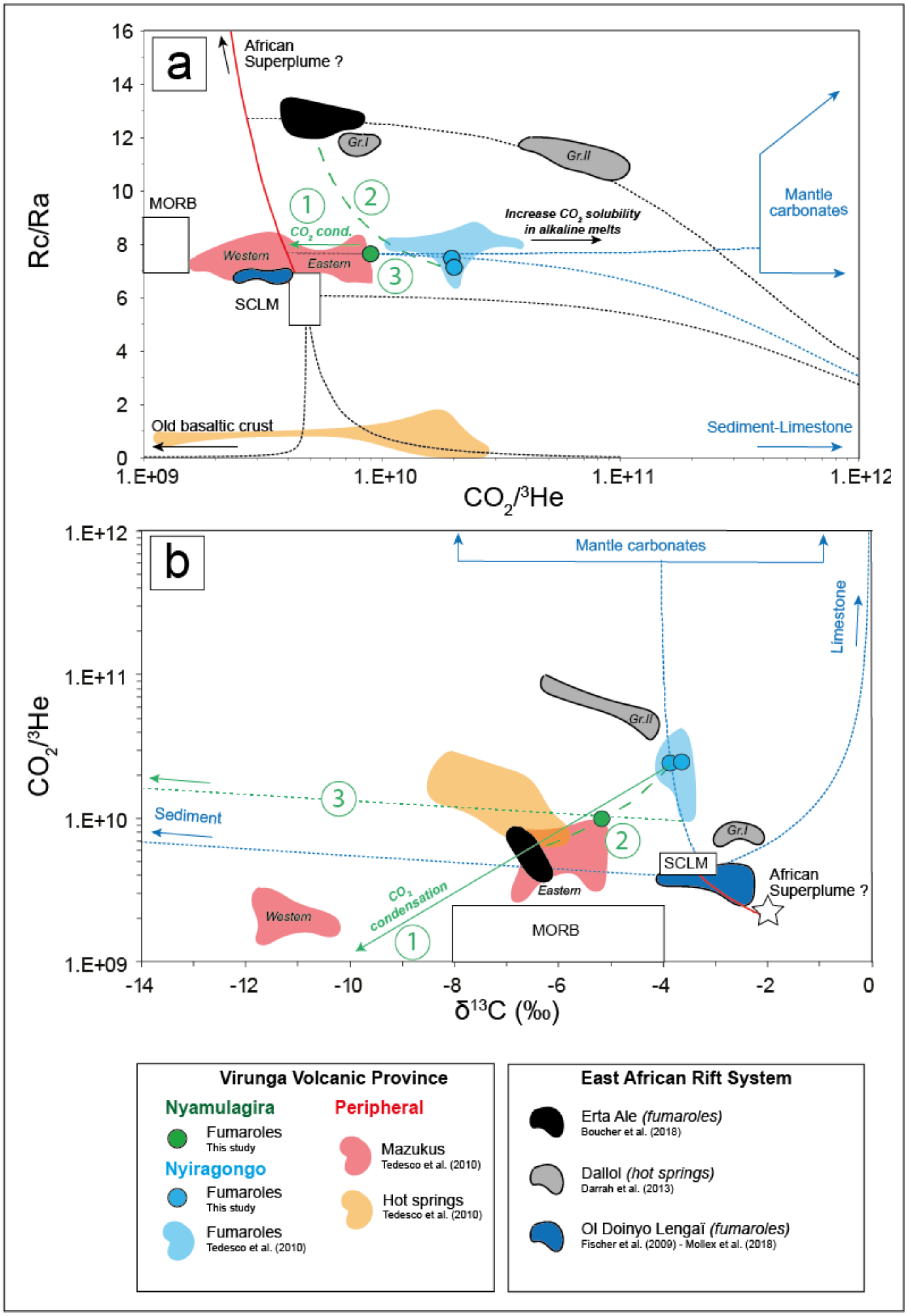


Fig. 5 (a) $CO_2/^3He$ vs. Rc/Ra and (b) $\delta^{13}C$ vs. $CO_2/^3He$. Continuous red line for mixing between an "African Superplume" component and the SCLM. Black and blue dotted lines for mixing with distinct crustal components or mantle carbonates (blue dotted lines are those discussed in the text

about the geochemical variability of gaseous emissions in the Virunga Volcanic Province with respect to the EARS). Green continuous, dotted and dashed lines relate to scenarios 1-2-3 discussed in the text and accounting for the chemical variability of gaseous emissions between Nyamulagira and Nyiragongo. CO_2 condensation process from Mook et al. (1974) computed with a temperature of 80°C similar to that measured in the fumaroles at Nyamulagira.