

**Microanalytical Investigations of Magma Sources, Evolution, Storage, and Ascent at
Nyiragongo and Nyamulagira**

by

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A dissertation accepted and approved in partial fulfillment of the
requirements for the degree of
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DISSERTATION ABSTRACT

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Doctor of Philosophy in Earth Sciences

Title: Microanalytical Investigations of Magma Sources, Evolution, Storage, and Ascent
at Nyiragongo and Nyamulagira

Processes occurring on the macro scale can be informed by processes occurring on the micro scale. In my dissertation, I show how we can understand volcanism through the lens of crystals and their inclusions, which through their volatile, major, trace, and isotopic signatures yield vital insights about magma sources, evolution, storage, and ascent. Petrologists have long used the chemistry of minerals and inclusions to understand magmatism, but some regions are more studied than others. In my dissertation, I focus on Nyiragongo and Nyamulagira volcanoes, located in the Western Branch of the East African Rift in a region called the Virunga Volcanic Province. Situated near the border of the Democratic Republic of the Congo and Rwanda, these volcanoes are highly hazardous, posing significant danger to growing populations in the region. By measuring the major, trace, and volatile elements, and oxidation states in olivine-hosted melt inclusions, I constrained primitive magma compositions, volatile budgets, and degassing processes in magmas at both volcanoes. Coupling these results with geochemical models, I show how magmas formed by melting of metasomatized mantle sources began crystallizing at crustal depths between 10 and 18 km, and degassed during ascent and eruption. Using the common phenocryst mineral olivine, I applied diffusion chronometry to estimate the time elapsed between protracted magma storage and eruption, showing that eruptions at flank cones occur months to weeks after magma mixing episodes. Combining the knowledge of volatile contents, storage depths, and mineral chemistry, I used measurements of H^+ in olivine to estimate magma ascent rates in the minutes and seconds prior to eruption, showing that rapid decompression rates of ($\sim 0.5 \pm 0.2$ MPa/s) facilitate explosive eruptions. This dissertation includes both published (currently in review) and unpublished co-authored material.

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What a privilege and opportunity it is to study the natural world. When I think about the journey taken by the rocks coming into the lab, I am continually humbled to play a role in untangling their complex histories. The fact that we can glean any insight at all about the nuances of this journey, is simply amazing.

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DEDICATION

To all those interested in the natural world

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CHAPTER I: INTRODUCTION

The East African Rift System (EARS), spanning over 5,000 km from Eritrea to Mozambique, is a prime example of modern continental rifting. For tens of millions of years, crustal thinning has gradually formed expansive rift valleys, lakes, and active volcanoes. Of the geologic regions experiencing rifting, the Archaean Tanzanian Craton is the most resistant to this change. Ranging from 170-200 km thick, these highly metasomatized intrusive rocks bifurcate the margin in its center, splitting the Western and Eastern Branches around its borders. In these regions of the EARS, melts generated in or interacting with sub-lithospheric mantle metasomatized by billions of years of geologic time yield globally distinctive magmatic compositions. In the Western Branch, three volcanic provinces (Toro-Ankole, Virunga, and South Kivu) produce exceptionally silica-undersaturated and alkalic magmas, the origins of which are still debated. Within this region, the Virunga Volcanic Province, situated on the borders of Democratic Republic of Congo, Rwanda, and Uganda, is home to the most active volcanoes in the EARS—Nyiragongo and Nyamulagira.

Located less than 15 km apart from one another, Nyiragongo, a stratovolcano, and Nyamulagira, a shield volcano, form the backdrop of the rapidly growing cities of Goma and Gisenyi and surrounding villages. In this region of over 1.2 million people, past and present geopolitical unrest fueled by a dark history of colonial exploitation has driven many civilians to seek safety in the Goma metro area, increasing the population exposed to volcanic hazards. Volcanic eruptions at Nyiragongo, most recently occurring in 1977, 2002, and 2021, have led to hundreds of deaths and thousands left homeless, and has overall served to destabilize an already geopolitically fragile region. While erupting seldomly in populated areas, Nyamulagira erupts even more frequently than Nyiragongo, creating lava flows >20 km in runout length.

In the past century, eruptions from both volcanoes have predominantly consisted of summit lava lake activity or near-summit (<10 km from the summit) lava effusions. This is not the only type of eruption, however, as the presence of >100 flank scoria and tuff cones show that both volcanoes have experienced small-volume explosive flank eruptions

>25 km from the main edifices. These high MgO eruptions are comparatively understudied in the petrologic record, but pose exceptional hazards due to their close proximity to population centers and potential of interacting explosively with the nearby waters of Lake Kivu.

At these understudied volcanoes, magmatic mysteries remain regarding the sources, storage, and eruption of magmas. My dissertation builds on our understanding of these processes from a microscopic perspective, using crystals and their melt inclusions as windows into magmatic systems. Melt inclusions, tiny blebs of magma entrapped in growing crystals, can serve as a unique window into the compositional history of magmas at depth, retaining the signatures of volatiles typically degassed during eruption. Their olivine crystalline hosts also serve as a unique record of magma storage, recording conditions of crystallization and storage within their compositional zones.

Through measuring micron-scale features in melt inclusions, minerals, and volcanic glasses from Nyiragongo and Nyamulagira tephra, my dissertation seeks to answer the following questions:

1. *What are the sub-crustal sources of magmas?*
2. *At what depths are magmas stored in the crust?*
3. *How long before a new eruption would there be geophysical signals of unrest?*
4. *At what rate do magmas ascend to the surface once an eruption has started?*
5. *How do magma degassing processes influence surficial volcanic gas emissions?*

In Chapter II, I use the volatile, major, and trace elemental concentrations of primitive olivine-hosted melt inclusions to investigate the volatile sources, magma storage depths, and degassing processes occurring at both Nyiragongo and Nyamulagira. This chapter was coauthored with Paul J. Wallace (University of Oregon), Kenneth W.W. Sims (University of Wyoming), D. Matthew Sublett (Virginia Polytechnical Institute and State University), and Robert J. Bodnar (Virginia Polytechnical Institute and State University) and is in review at the journal *Earth and Planetary Science Letters*.

With analyses of over 100 melt inclusions (MI) and combining datasets from eight analytical techniques this is the largest and most holistic melt inclusion dataset generated from the East African Rift System. Analyses of magmatic CO₂ in MI (including both vapor bubbles and glasses) reach up to 1.3 wt% and 0.9 wt% CO₂ for Nyiragongo and Nyamulagira, respectively. Water concentrations measured in MI glasses range from 0.7-1.6 wt % H₂O in primitive samples and 0.2-0.4 wt % H₂O in more evolved samples. Sulfur concentrations in MI are as high as 3100 ppm at Nyiragongo and 2500 ppm at Nyamulagira. Through multivariate statistical analysis, we show how melt inclusions can be compositionally fingerprinted and attributed to different volcano sources. Constraints from volatile solubility modeling indicate initial crystallization of the most primitive melts at depths of 10-18 km below vent surfaces, which align well with seismic swarms recorded at Nyiragongo. Primary CO₂ estimates in source magmas from geochemical proxies based on published experimental data range 6.0±2.5 wt% for Nyiragongo and 4.4±2.5 wt% for Nyamulagira. To produce volatile and major elemental compositions, a source involving clinopyroxene, phlogopite, and amphibole is necessary, likely hosted in lithospheric metasomes, which are domains or highly veined regions of the lithospheric mantle that have been strongly affected by fluids or silicate melts in the geologic past. One or more carbonate minerals, hosted in either metasomes or surrounding peridotite, is also required to produce the high magmatic CO₂ concentrations and likely the high melt CaO concentrations as well. Moving from the source to the surface, we use the CO₂, H₂O, and S concentrations measured in MI to forward model degassing paths and compare these with measured surficial gas emissions. Our models show that gasses emitted from the lava lakes are fed by evolved magmas with high initial CO₂.

The interpretations in Chapter II are fueled by numerous analytical techniques, geochemical models, and comparisons to literature data. Chapter III presents additional data, modeling, and supplementary discussion that is important to the work presented in Chapter II. The unusual compositions and complexities of magma mixing, fractional crystallization, and other magmatic processes in the flank cones of Nyiragongo and Nyamulagira required a careful check of commonly used modeling tools and methods.

In Chapter IV, I use major and minor element zonation in olivine to assess the timescales between magma mixing events and eruption at the flank cones of Nyiragongo

and Nyamulagira. Tephra samples from different eruptions show ranges in olivine composition, which are indicative of at least three distinct magma reservoirs beneath Nyiragongo and Nyamulagira in which olivine forsterite content correlates with both depth and distance of eruptive vents from the summit. Most olivine phenocrysts have normal zoning, consistent with the interpretation that primitive melts with high Fo olivine intruded into a more evolved melt, triggering eruption. Constraints from diffusion modeling transects of Fe-Mg (both measured and approximated with backscattered electron [BSE] imagery) and Ni in olivine suggest magmas reside in the shallow crust 14-24 days between magma mixing events and eruption. Variations in H^+ concentrations in olivine phenocrysts record processes occurring on a shorter timescale, yielding information about ascent processes once an eruption had started. By applying a diffusion model that integrates degassing in its boundary conditions, I find that decompression occurred at 0.5 ± 0.2 MPa/s, aligning with previous estimates of highly explosive basaltic eruptions.

CHAPTER II: MAGMA SOURCES, CRUSTAL STORAGE DEPTHS, AND DEGASSING OF ALKALIC, CO₂-RICH MAGMAS AT NYIRAGONGO AND NYAMULAGIRA VOLCANOES, DEMOCRATIC REPUBLIC OF THE CONGO

This work is in review in the journal *Earth and Planetary Science Letters* with Lissie Connors as lead author, and co-authors Paul J. Wallace (University of Oregon), Kenneth W.W. Sims (University of Wyoming), D. Matthew Sublett (Virginia Polytechnical Institute and State University), and Robert J. Bodnar (Virginia Polytechnical Institute and State University). This project scope was developed by Kenneth W.W. Sims, Paul J. Wallace, and Lissie Connors. Sample collection was led by Kenneth W.W. Sims. Data collection was led by Lissie Connors and D. Matthew Sublett. Writing was led by Lissie Connors and Paul J. Wallace. All authors were involved in the editing process.

1. Introduction

Extension in the East African Rift System (EARS) generates volcanism with a diverse range of eruptive behaviors, compositions, and hazards. Nyiragongo and Nyamulagira, in the Democratic Republic of the Congo, are two of the most active volcanoes in the EARS, posing substantial risk to nearby populations (Pouclet and Bram, 2021). Only 15 km apart, their chemical and isotopic compositions and physical characteristics are profoundly different, with Nyiragongo erupting some of the most silica-undersaturated and least viscous lavas on Earth (melilitite, nephelinite; Demant et al., 1994; Platz et al., 2004; Molendijk et al., 2024), and Nyamulagira erupting basanites and tephrites (Aoki et al., 1985; Chakrabarti et al., 2009) similar to volcanic systems in the surrounding Virunga Volcanic Province (e.g. Mikenno, Bufumbira). Despite their potential hazards, flank eruptions at these volcanoes are poorly studied (Pope et al., 2016).

Estimates of CO₂ fluxes in the Eastern Branch (71 +/- 33 Tg/a: Lee et al., 2016) and Main Ethiopian Rift (4-33 Tg/a: Hunt et al., 2017) highlight the importance of the EARS in the global carbon cycle. At Nyiragongo and Nyamulagira, significant CO₂ and SO₂ emissions rank these edifices among the strongest volcanic emitters on Earth (Fischer et al., 2019). Sources of CO₂ released from continental rifts have been attributed to carbon

sequestered in lithospheric mantle by carbon-rich silicate melts related to mantle convection, plumes, and subduction (e.g. Foley and Fischer, 2017), but petrologic constraints on magmatic CO₂ in the EARS remain sparse. Petrologic determinations of the concentrations of magmatic volatiles are essential for deciphering magmatic sources, storage conditions, and surface gas emissions at Nyiragongo and Nyamulagira.

2. Samples and Methods

We analyzed 118 melt inclusions (MI) from 7 tephra samples (Fig. 1) erupted at cones along the flanks of Nyiragongo (DRC 01T [Mugara], 17T [Lac Vert], 31T [NE Tephra], 39T [Kirunga]), and Nyamulagira (DRC 21T [Nzulu], 22T [Kituharu], 23T [Shove]) and one tephra sample from inside the summit crater of Nyamulagira (DRC 06T), all of which were collected during a 2015 field expedition (Phillips, 2015). Tephra were collected from several prominent fissure systems where flank vents are radially aligned from Nyiragongo's central edifice (Fig. 1), including the NE-SW trending Rushayo chain (17T [Lac Vert], 39T [Kirunga]), N-S trending Mudjoja-Bushwaga chain (01T [Mugara]), and E-W trending Nyamushwa chain (31T [NE Tephra]). At Nyamulagira, many proximal vents are concentrated along faults on the NE and SW flanks, but tephra from this study are from vents further south (21T, 22T, 23T). Farther from both edifices and close to the shores of Lake Kivu, vent alignments are less distinct.

Olivine phenocrysts are present in both primitive and evolved Virunga magmas, making their trapped melt inclusions ideal tracers of magmatic evolution across a broad compositional range. We determined CO₂ density in MI vapor bubbles using Raman spectroscopy. Volatiles in MI glasses (H₂O, CO₂, S, F, Cl) were analyzed by Secondary Ion Mass Spectrometry (SIMS). We combined the SIMS and Raman CO₂ results to calculate the total CO₂ concentration of MI at the time of trapping. Before SIMS analysis, a subset of MI were analyzed for Fe and S redox state by synchrotron-based micro-X-ray absorption near edge structure (XANES) spectroscopy. Given the susceptibility of MI to photo-oxidation and -reduction, we employed methodologies from Lerner et al. (2020), including defocused beams, repeated rapid scans, and low incident fluxes for S-XANES. Major elements in MI glasses, matrix glasses, and host olivine crystals were analyzed by

electron microprobe (EPMA), and trace elements in MI were analyzed using laser ablation inductively coupled mass spectrometry (LA-ICP-MS). We accounted for effects of post-entrapment crystallization and diffusive Fe-Mg exchange of MI with the olivine host using MIMiC (Rassmussen et al., 2020). Tables with all analytical data and detailed descriptions of analytical methods, uncertainties, MIMiC corrections, and the CO₂ calculations can be found in the Supplementary Materials.

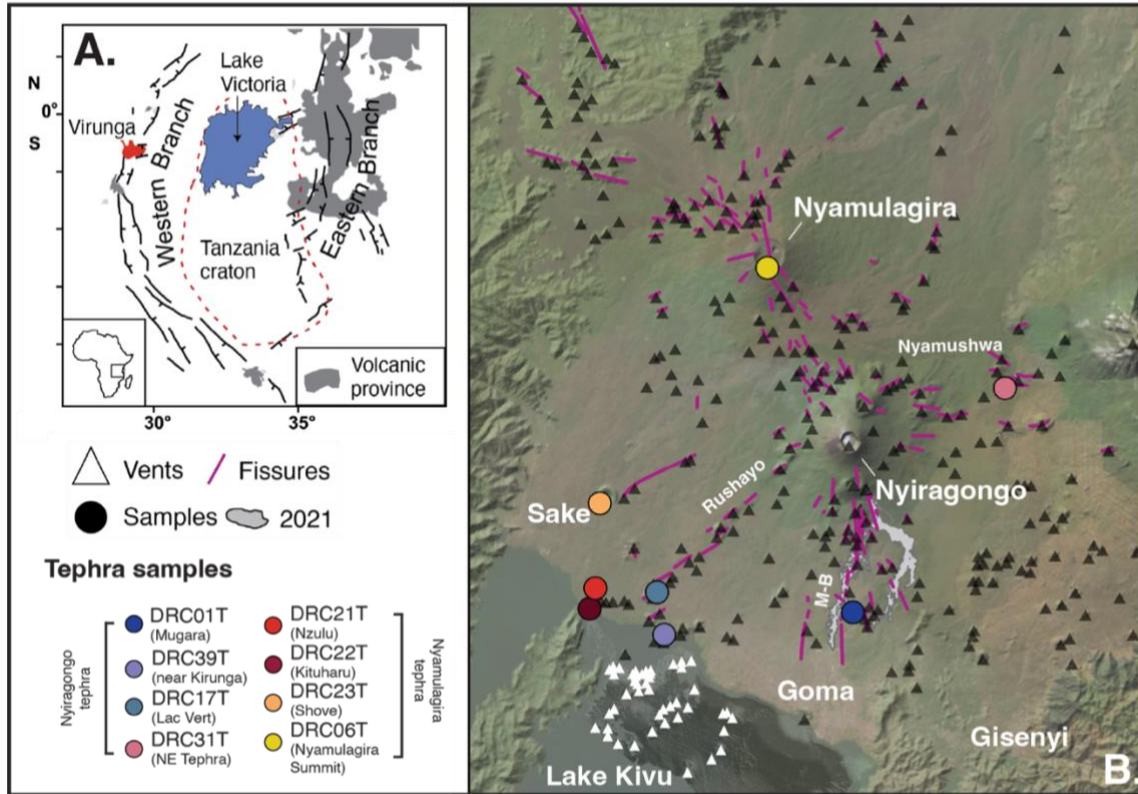


Figure 1. A. Map of the East African Rift, with Virunga Volcanic Province indicated in red. B. Locations of tephra samples. Flank vent and fissure locations are from Smets et al. (2014); lake bathymetry is from Ross et al. (2014). Black triangles indicate subaerial vents, white triangles indicate vents along the current floor of Lake Kivu. Fissure systems shown by purple lines are from Demant et al. (1994). major fissures from Nyiragongo are labelled (Rushayo, M-B [Mudjoga-Bushwaga], Nyamushwa).

3. Results

3.1 Sample petrography and geochemistry

All tephra samples analyzed in this study are vesicular and glassy, with varying abundances of olivine. Samples associated with phreatomagmatic eruptions (21T, 22T,

17T) exhibit the glassiest textures and lowest microlite number densities. Tephra from the Nzulu (21T) and Shove (23T) cones and the NE Tephra (31T) are alkali basalts, with phenocrysts of olivine and clinopyroxene (Fig. 2; Table S1). Tephra from Kituharu (22T), with slightly lower SiO₂, is classified as basanite. The Nyamulagira Summit tephra (06T) is tephrite, with phenocrysts of clinopyroxene, plagioclase, and rare olivine. With abundant olivine, clinopyroxene and rare melilite phenocrysts, the Mugara (01T) and Kirunga (39T) samples fall within a compositionally diverse field of “olivine basalts” as defined by Molendijk et al. (2024). Lac Vert (17T), the most evolved tephra sample, is classified as nephelinite with phenocrysts of nepheline, melilite, clinopyroxene, and olivine. Lavas from Nyiragongo form a consanguineous group related by varying degrees of fractional crystallization, olivine accumulation (at MgO>12 wt%), and leucite and/or nepheline accumulation (at MgO<5wt%; Molendijk et al., 2024). For simplicity and clarity, we will refer to lavas and tephra from flank cones and both volcanic edifices with Fo $\geq$ 85 as more primitive and Fo<85 as more evolved.

3.2 Compositions of melt inclusions and olivine hosts

Olivine phenocrysts are generally euhedral and in most samples are normally zoned along their outer 100 μ m. Four samples (Shove [23T], Kituharu [22T], Lac Vert [17T], and NE Tephra [(31T)]) also contain some olivine with reverse zoning in their outer $\sim$ 100 μ m. Most tephra samples have high-Mg olivine (Fo₈₅₋₉₁; Fig. S9), whereas olivine from the Nyamulagira summit cone are more Fe-rich (Fo₇₆₋₇₈). Olivine from the Lac Vert tephra are the most heterogeneous in composition (Fo₇₄₋₉₀) and show multiple zoning populations. Despite this diversity, rim compositions from Lac Vert converge at Fo₇₅.

Compositions of bulk tephra and matrix glasses from our sample suite overlap with published whole-rock data (Figs. 2, 6). Restored major element compositions of MI have 39-47 wt% SiO₂ and overlap extensively with Nyamulagira whole-rock samples. Relatively fewer MI have compositions similar to Nyiragongo whole-rocks, and none overlap with the very high alkali contents typical of evolved Nyiragongo magmas. We

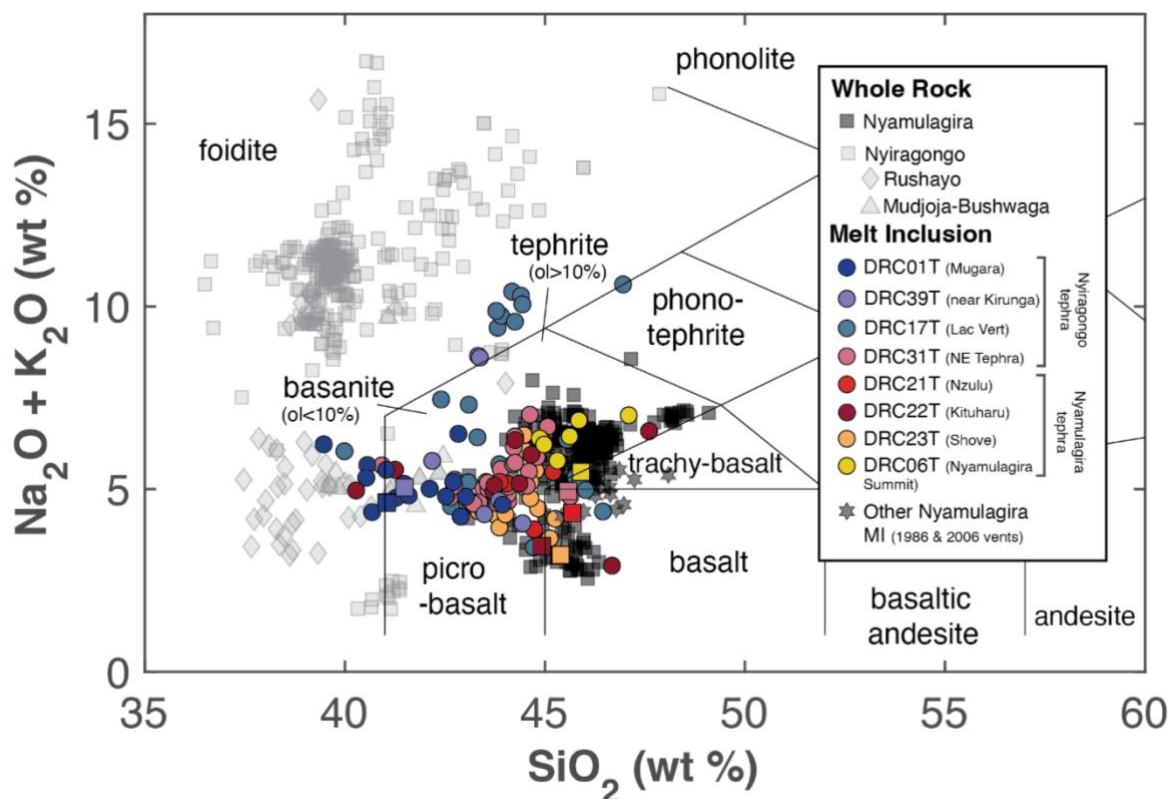


Figure 2. Total alkalis versus silica (TAS) diagram showing whole-rock data from Nyiragongo (light gray squares, diamonds and triangles) and Nyamulagira (dark gray squares). Bulk tephra from this study are shown as colored squares and melt inclusions as colored circles. Black hexagrams are MI data from tephra erupted from Nyamulagira in 1986 and 2006 from Head et al. (2011).

discuss MI compositional variations further in section 4.1, using a more rigorous method to assess whether individual MI formed from Nyiragongo- or Nyamulagira-type melts.

3.3 CO_2 in MI vapor bubbles

Most MI in this study contained a single vapor bubble. The samples from Shove (23T) and the NE Tephra (31T) have the most bubble-free inclusions (30-40% of MI). Of the 103 vapor bubbles analyzed using Raman Spectroscopy, 98 contained detectable CO_2 . The only MI bubbles with no detectable CO_2 were those from the Nyamulagira Summit Cone (06T). Room temperature densities of CO_2 range from 0.04-0.48 g/cm³, with a

median value of 0.22 g/cm³ (Fig. 3). Densities >0.22 g/cm³ indicate coexisting liquid+vapor in the bubble, which was confirmed petrographically. These inclusions were remeasured at 31.1°C (above the critical temperature of CO₂) to homogenize the liquid and vapor phase (Sublett, 2020). Of the 103 analyzed bubbles, 20 showed a broad peak at 1089 cm⁻¹, indicative of a carbonate phase along the vapor bubble wall. Vapor bubbles with observed carbonate peaks show similar CO₂ densities to those without observed peaks, and therefore there is no correlation of total reconstructed CO₂ with presence or absence of carbonate. For the 20 bubbles with carbonates, only 3 of the MI glasses were analyzed for volatiles by SIMS due to sample attrition during preparation.

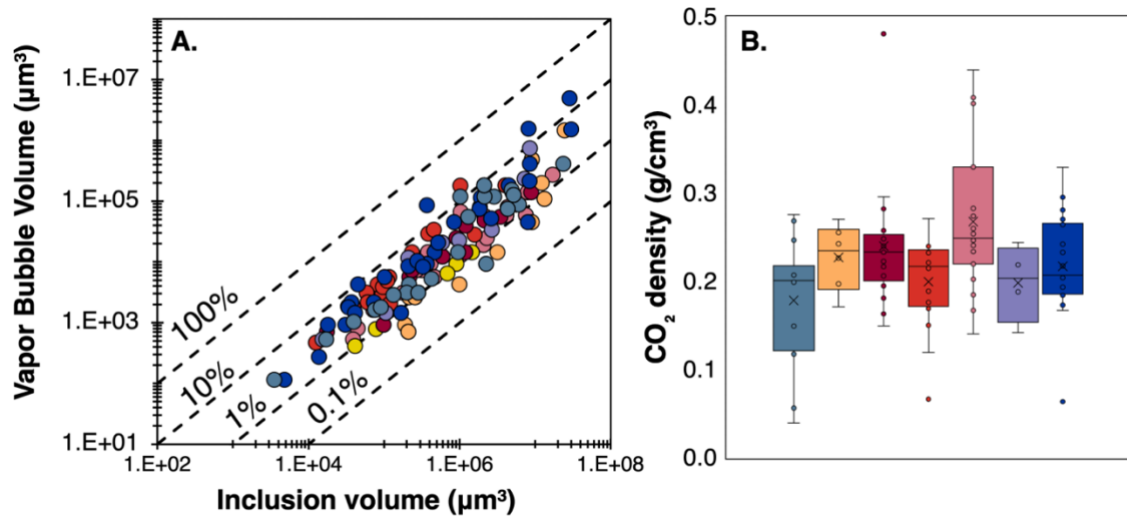


Figure 3. **A.** Measured volumes of melt inclusions and their vapor bubbles. Symbols as in Fig. 2. Dashed lines show the volume percentage of vapor bubbles relative to total MI volume. MI from this study have bubble vol% values of 0.5-12%. **B.** Raman-measured vapor bubble CO₂ densities. Densities over 0.22 indicate the presence of liquid and vapor in the bubble and were remeasured at 31.1°C to homogenize the phases according to Sublett (2020). Nyamulagira summit sample (06T) did not show detectable CO₂ in any vapor bubbles. Circles denote individual data points, x's denote averages. Small circles indicate individual data points; x's indicate mean CO₂ densities; horizontal lines inside boxes indicate median CO₂ densities; upper and lower limits of boxes indicate upper and lower quartiles; and whiskers extend to minimum and maximum CO₂ densities.

3.4 Volatiles (CO₂, H₂O, S, Cl, F) in MI glasses

Analyses of MI glasses yield CO₂ concentrations up to 1 wt% (Table S5). Vapor-bubble restored CO₂ concentrations in MIs reach up to 1.3 wt% (Fig. 4), with the highest

values in MI from the Mugara tephra (01T). We compared Raman-restored CO_2 concentrations with MIMiC-restored CO_2 values. The comparison shows good agreement for $\text{CO}_2 < \sim 5000$ ppm but increasingly divergent values at higher concentrations, with maximum values of ~ 2 wt% CO_2 estimated from MIMiC (Fig. S11).

The highest H_2O concentrations in MI (~ 1.6 wt%) were found in the Shove cone (23T). The Mugara, Kirunga, Nzulu, and Kituharu cones tend to have slightly lower H_2O (average: 0.93 wt% H_2O) and high bubble-corrected CO_2 , whereas the Shove and NE

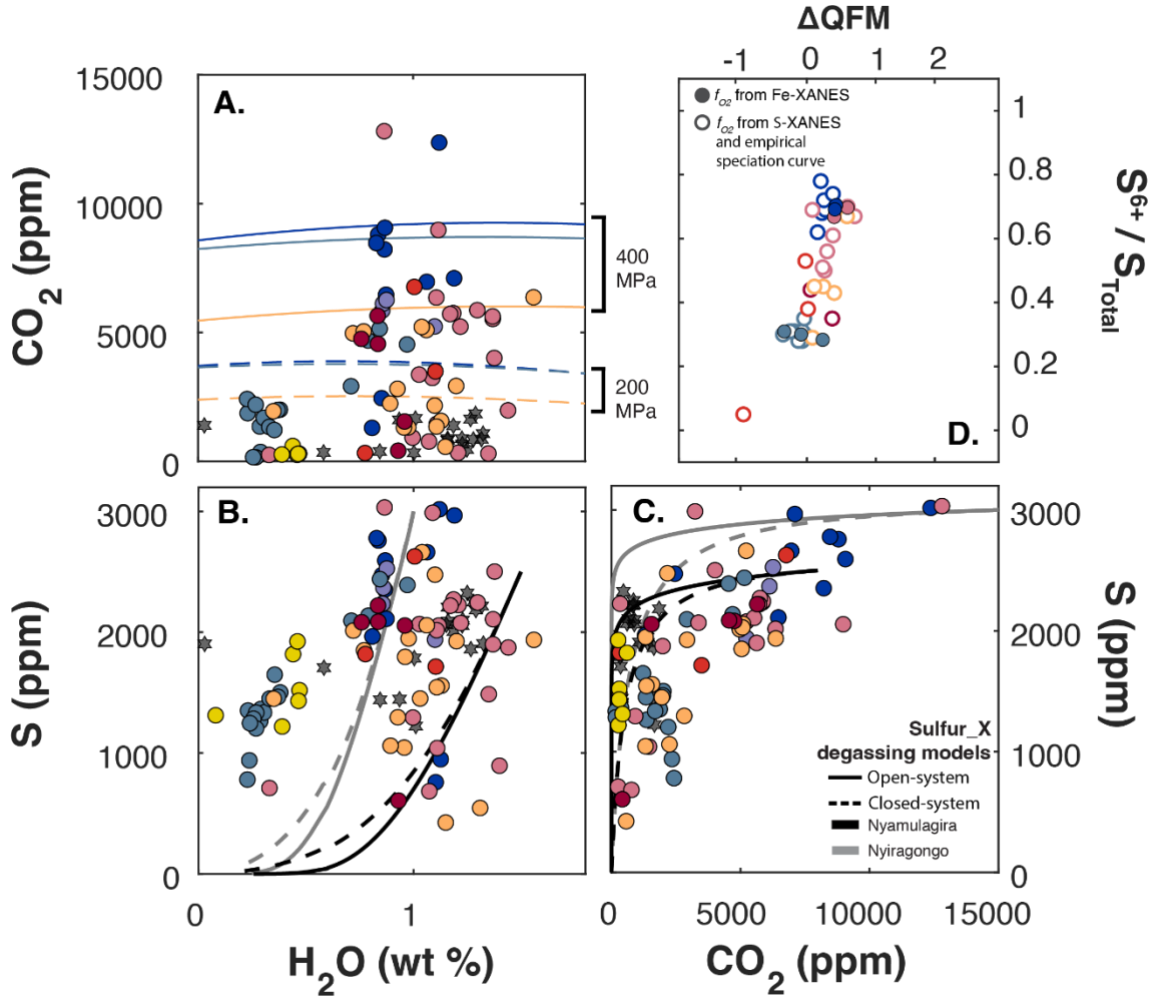


Figure 4. Concentrations of CO_2 (vapor bubble+glass), H_2O (glass), and S (glass) in melt inclusions. Symbols as in Fig. 2. Black hexagrams show bubble-free melt inclusions from near -summit Nyamulagira tephra (Head et al., 2011). **A.** Curves represent saturation isobars for average MI compositions from Mugara (01T, dark blue), Shove (23T, orange), and evolved MI from Lac Vert (light blue), at 400 MPa (solid) and 200 MPa (dashed), modeled using MagmaSat. **B,C.** open- and closed-system degassing curves modeled using Sulfur_X (Ding et al., 2023) for Nyiragongo (black) and Nyamulagira (gray) compositions. **D.** $\text{S}^{6+}/\Sigma\text{S}$ values measured by XANES versus $f\text{O}_2$ determined from XANES-measured $\text{Fe}^{3+}/\Sigma\text{Fe}$ (solid symbols) or inferred from $\text{S}^{6+}/\Sigma\text{S}$ as described in the Supplementary Materials.

Tephra tend to have slightly higher H₂O (average 1.1 wt%) and lower CO₂. The lowest CO₂ and H₂O concentrations are found in low-Fo olivine from Lac Vert (17T; average: 0.28 wt% H₂O, 1470 ppm CO₂) and Nyamulagira Summit cone (average: 0.44 wt% H₂O, 345 ppm CO₂).

Fluorine and chlorine concentrations are correlated with K₂O (Fig. S15). High-MgO MI have ~700 ppm and ~500 ppm Cl. At lower MgO and higher K₂O, MI reach up to 2500 ppm F and 1550 ppm Cl. Matrix glasses overlap with the higher end of the MI Cl range and extend to even higher Cl values.

Sulfur concentrations are highest (up to 3100 ppm) in the Mugara sample (01T), with some MI from the NE Tephra (31T) reaching similarly high values. Concentrations of S versus CO₂ show considerable scatter, and the highest S concentrations are generally found in MI with the highest CO₂ (Fig. 4). Comparison of S versus H₂O shows a bifurcating pattern where the majority of MI form a scattered vertical array with highly variable S, and A subset (mostly evolved MI from Nyamulagira summit [06T] and Lac Vert [17T]) show positively correlated values. Matrix glasses generally have lower S concentrations than MI. Interestingly, matrix glasses from Lac Vert show the highest S concentrations (~1400 ppm), similar to values for the lower MgO melt inclusions, likely because quenching during phreatomagmatic eruption inhibited S degassing. Comparison of our data with magma degassing models is discussed in section 4.3.

3.5 Fe and S redox state in MI glasses

Fe-XANES spectra were collected on a subset (n = 11) of MI from the Mugara (01T), NE Tephra (31T), and Lac Vert (17T) samples. Centroid values of spectra normalized to the incident flux were converted into Fe³⁺/ΣFe using an updated calibration from Muth and Cottrell (2023). Measured Fe³⁺/ΣFe values are 0.21-0.22 (Mugara), 0.19-0.21 (NE Tephra), and 0.15-0.18 (Lac Vert). Using Kress and Carmichael (1990), we converted Fe³⁺/ΣFe into *f*_{O₂} values of QFM+0.4 (Mugara), QFM+0.2 to 0.5 (NE Tephra) and QFM-0.1 to -0.5 (Lac Vert; Fig. 4d). A larger subset (n = 34) of MI was analyzed by S XANES. For MI without evidence of beam damage, S⁶⁺/ΣS was determined from XANES spectra using Lerner et al. (2020), yielding S⁶⁺/ΣS values of 0.6-0.8 (Mugara

[01T]), 0.5-0.7 (NE Tephra [31T]), 0.3-0.4 (Lac Vert [17T]), 0.4-0.6 (Nzulu [21T]), 0.3-0.4 (Kituharu [22T]), and 0.3-0.6 (Shove [23T]; Fig. 4d). Further details on XANES measurements and estimation of f_{O_2} values for MI with S-XANES but no Fe-XANES measurements are in section 2.2 of the Supplementary Materials.

4. Discussion

4.1. Spatial variations in magma composition and chemical fingerprinting of melt inclusions.

Spatial variations of lava and tephra geochemistry in the Virunga Volcanic Province (VVP) have been investigated by Barette et al. (2017). Using Principal component analyses (PCA), they highlight Nyiragongo as unique geochemically within the VVP, and on a finer scale, affirmed compositional differences between the Rushayo, Mudjoja-Bushwaga, and Nyamushwa chains (Fig. 1). To assess whether individual MI formed from either Nyiragongo or Nyamulagira magmas, we adopted a similar statistical approach (Fig. 5a) using a compilation of whole-rock data from each volcano. In our analysis, two principal components can reasonably differentiate Nyiragongo and Nyamulagira compositions. The first principal component (PC1) has high MgO and low K₂O and Na₂O, whereas the second (PC2) has higher SiO₂ and Al₂O₃ and lower FeO^T and CaO. For primitive compositions, the largest differences are between SiO₂ (see Fig. 2) and Al₂O₃ (higher at Nyamulagira, lower at Nyiragongo) and FeO^T and P₂O₅ (lower at Nyamulagira, higher at Nyiragongo). When expanded to all Virunga volcanoes, Nyamulagira compositions closely resemble rocks at Gahinga, Visoke, Mikenno, and Bufumbira. On a finer scale, high-Mg whole-rock compositions show gradational differences between high PC2 primitive distal Nyamulagira cones (22T, 21T), the N-S Mudjoga-Bushwaga chain (01T), and the low PC2 Rushayo chain (Fig. 5). These differences can most clearly be seen in systematic P₂O₅ variations (Fig. 6). High-Mg Rushayo chain lavas have been modeled as parental to main edifice Nyiragongo lavas (Fig. 6; Molendijk et al., 2024; Platz et al., 2004).

After defining Nyiragongo- and Nyamulagira-type compositional fields, we apply this fingerprinting framework to our MI (Fig. 5b), designating compositions as either Nyiragongo- or Nyamulagira-type. The occurrence of MI from the same tephra in different

compositional fields suggests magma mixing at depth. Only the Mudjoja-Bushwaga chain Mugara tephra (01T) has dominantly Nyiragongo -type MI. For the Kirunga tephra (39T) offset southeast from the Rushayo-chain, ~50% of MI are Nyiragongo type. Interestingly, the NE tephra sample (31T) from the Nyamushwa chain shows 90% Nyamulagira-type MI. Few Nyamushwa chain whole-rock samples have been analyzed, but the limited published data indicate this chain is compositionally similar to Nyamulagira.

Cones along the western shores of Lake Kivu (21T, 22T), although geographically closer to Nyiragongo, have Nyamulagira-type MI compositions. Primitive MI from tephra collected near Lac Vert (17T) also show Nyamulagira-type composition in contrast to

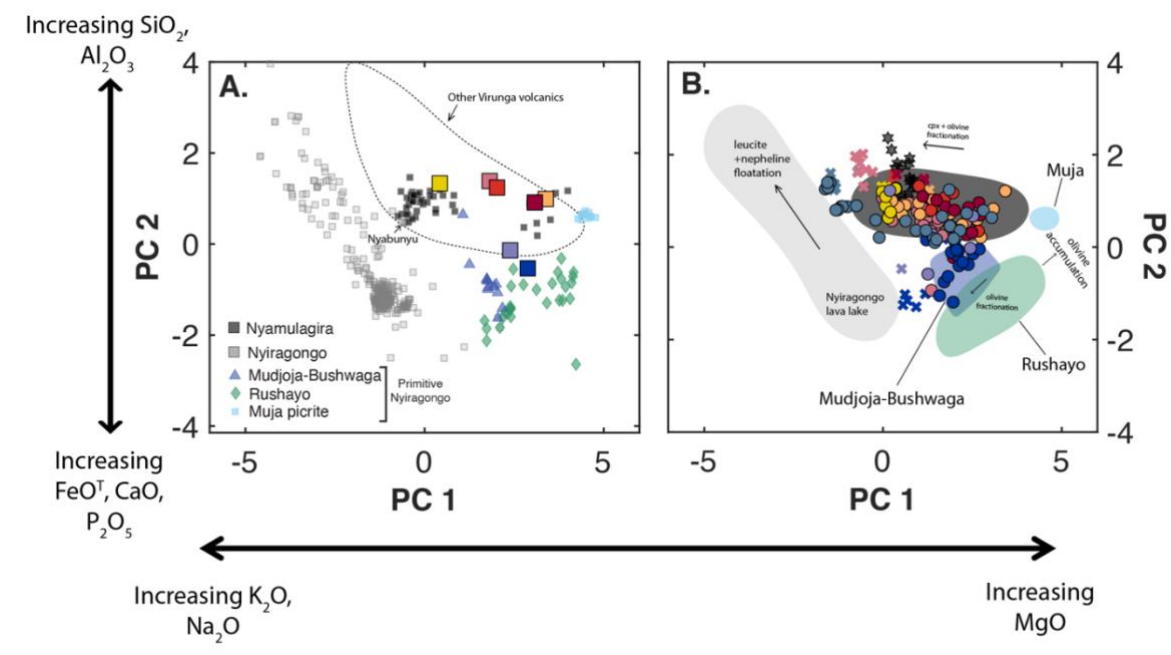


Figure 5. Principal components of whole-rock, MI, and matrix glass data as discussed in the text. Symbols are the same as in Figure 2, with Rushayo and Mudjoja-Bushwaga chain samples in blue and green, respectively. **A.** Whole-rock samples used to outline principal component compositional fields. **B.** Principal component fields compared with MI and matrix glasses (x's). Symbols for MI as in Figs. 2, 4. Whole-rock data from Aoki et al. (1984); Aoki et al. (1985); Chakrabarti et al. (2009); Head et al. (2011); Phillips (2015); Poulet et al. (2016); Minissale et al. (2019); Minissale et al. (2022); Molendijk et al. (2023; 2024); Kamate Kaleghetso et al. (2025). Additional Nyamulagira MI data from Head et al. (2011). The Muja picrite is a cone along the Mudjoja-Bushwaga chain that acts as a compositional outlier among vents. Its high MgO contents (>20 wt% MgO) and high modal olivine proportions suggest it has formed from olivine accumulation (Molendijk et al., 2024).

highly alkalic Lac Vert lavas (Chakrabarti et al. 2009; Molendijk et al. 2024). evolved MI from tephra 17T have high Na_2O , K_2O , and SiO_2 similar to bulk rock samples from Nyabyunyu, an edifice 2 km to the east. While we plot these MI as Nyiragongo-type MI, their classification remains somewhat enigmatic.

In summary, based on PCA and spatial patterns, we suggest that the compositional variability of primitive compositions at Nyiragongo is influenced by small -scale source heterogeneities (see section 4.6), whereas compositions at Nyamulagira more broadly reflect mantle sources throughout the Virunga Volcanic Province. The Kameronze fault system, running SW-NE along Nyiragongo's southwestern flank, has been invoked as a canonical boundary between Nyiragongo and Nyamulagira magmatic systems (Pouclet and Bram 2021), but fingerprinting of our MI dataset shows that magmas in this region may interact with one another.

4.2 Magma evolution at Nyiragongo and Nyamulagira

Nyamulagira-type MI and tephra compositions overlap whole-rock data (Fig. 6), with MI crossing compositional gaps exhibited by bimodally distributed MgO values of lavas. Fractional crystallization models in MELTS involving dominantly olivine+clinopyroxene successfully reproduce the major element trends, including the compositions of evolved summit cone and lava lake compositions (Fig. 6; see Supplementary Materials section 4.3). The highest-Mg Nyamulagira MI are from distal flank cones (Nzulu [21T]; Kituharu [22T]; Shove [23T]; and NE Tephra [31T]), whereas MI from near summit 1986 and 2006 tephra (Head et al., 2011) and the Nyamulagira summit cone [06T] have progressively lower Mg values. Correlations between differentiation extent and proximity to the edifice align well with interpretations of Nyamulagira's plumbing system (Pouclet and Bram, 2021).

Nyiragongo-type MI overlap with primitive to intermediate whole-rock compositions (5.5-12.5 wt% MgO) from both Mudjoga-Bushwaga and Rushayo chains for all major elements except P_2O_5 , as noted above. Our MI P_2O_5 concentrations most closely resemble Mudjoga-Bushwaga primitive samples. The MI in lower-Fo olivine from Lac Vert (17T) are more evolved (3.5-6 wt% MgO) and plot close to but are distinct from main

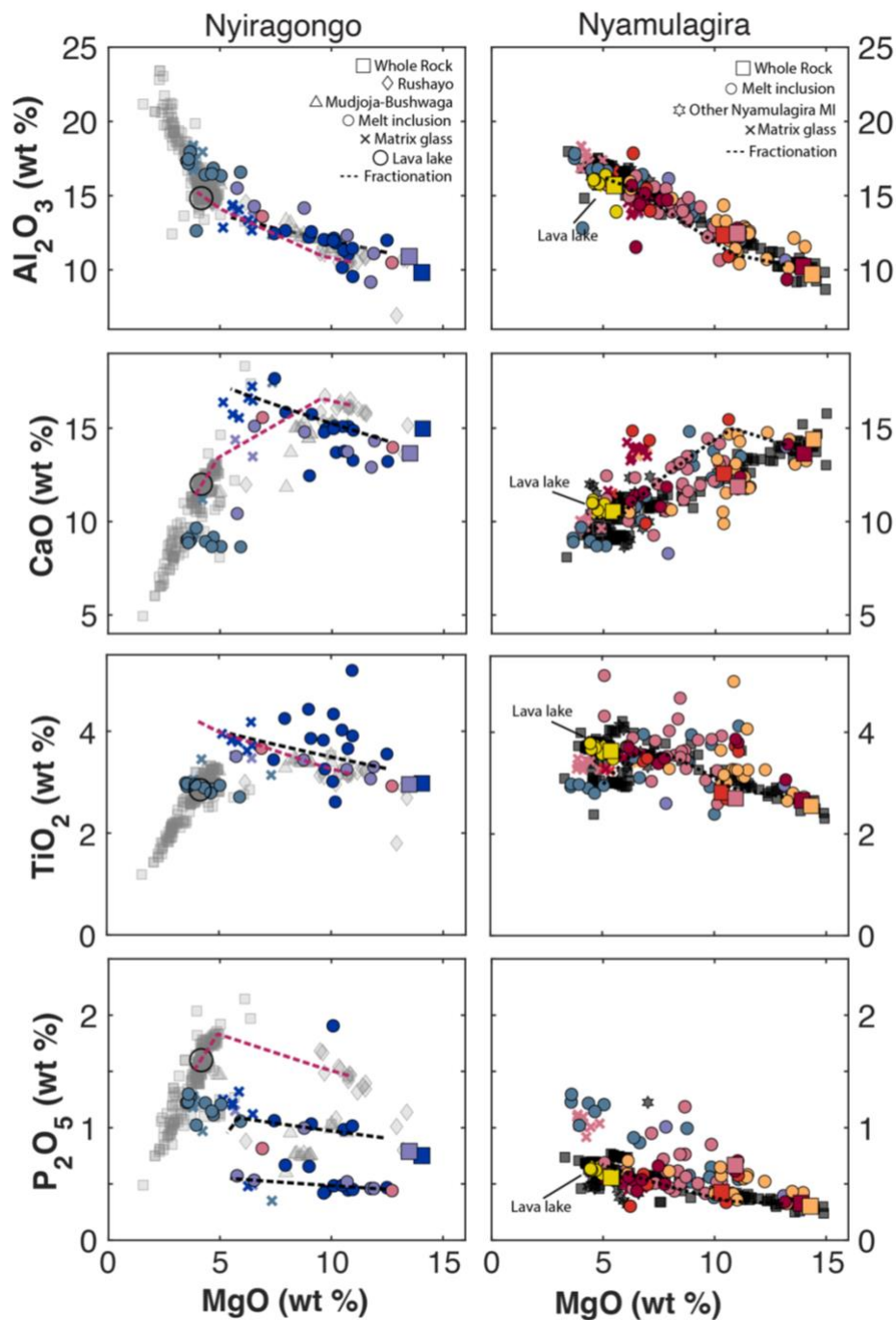


Figure 6. Major element compositions of whole-rock, MI, and matrix glasses, separated into Nyamulagira and Nyiragongo types based on principal component analysis. Symbols for MI as in Figs. 2, 4. Whole-rock data from references in Figure 5. Liquid line of descent for Nyiragongo from Molendijk et al. (2024) is shown in purple; MELTS-modeled (Gualda et al., 2012) liquid lines of descent for both volcanoes are shown in black (see section 4.2 in Supplementary Materials). Multiple fractional crystallization trends for P_2O_5 are modeled at Nyiragongo to show varying initial compositions.

Nyiragongo edifice and summit lava lake samples (Fig. 6). Fractional crystallization models show Nyiragongo magmas evolve from a ~10.8 wt% MgO parent melt (Molendijk et al., 2024), with early olivine, melilite, and Cr-spinel fractionation, followed by crystallization of clinopyroxene, nepheline, melilite, and apatite (Fig. 6). While Molendijk et al. (2024) interpret samples with MgO > ~12 wt% as affected by olivine accumulation,

Our MI and olivine data suggest parental melts for the Mudjoja-Bushwaga chain extend to 12.5 wt% MgO (Fo_{89.5}). Most of the major element compositional variation in Nyiragongo-type MI and matrix glasses can be explained by olivine-only fractional crystallization of parent melts with P₂O₅ similar to or lower than Mudjoja-Bushwaga values (Fig. 6).

4.3 Volatile concentrations, degassing, and sulfide formation

After accounting for CO₂ in both vapor bubbles and glass, MI contain up to 1.3 wt% CO₂ (Fig. 4), with the highest concentrations in the Mugara tephra (01T; Mudjoja-Bushwaga chain, dominantly Nyiragongo-type MI) and Two MI of Nyiragongo-type from the NE tephra (31T). MI with Nyamulagira-type compositions have maximum CO₂ values of ~0.9 wt%). These calculations do not account for potential carbonate phases present along bubble walls, which would increase the bubble-corrected CO₂ values.

Our sample suite has the second highest CO₂ concentrations in MI from the EARS. Elsewhere in the EARS, rehomogenized MI from Bufumbira have ≤1 wt% CO₂ (Hudgins et al., 2015), and MI from Lake Turkana have bubble-corrected CO₂ values ≤2240 ppm (Rooney et al., 2022). Further north, MI from the Main Ethiopian Rift (MER; Wong et al., 2023) have bubble-corrected CO₂ concentrations ≤5770 ppm, highlighting that CO₂-rich magmas are prevalent throughout the rift, even in subalkaline basaltic magmas.

The least degassed MI in our dataset have 0.7-1.5 wt% H₂O (Fig. 4), and values positively correlate with K₂O (Fig. S15a), indicating moderate H₂O increases during differentiation, with scatter likely caused by effects of diffusive loss. This range of H₂O contents is comparable to olivine-hosted MI with less silica-undersaturated compositions

in other regions of the EARS (Brounce et al. 2024; Wong et al., 2023; Rooney et al., 2022; Iddon & Edmonds 2020; Hudgins et al., 2015), but is a more restricted range compared to MI from ocean islands (DeVitre et al., 2023, and references therein), which reach up to 3.5 wt% H₂O (see Supplementary Materials).

Lower H₂O concentrations (0.3-0.44 wt%) in more evolved MI from Nyamulagira Summit and Lac Vert likely indicate magma had degassed before MI entrapment (Figs. 4, S15b). While low in H₂O and S, evolved Lac Vert MI contain 1200-2500 ppm CO₂ (Fig. 4). These values likely result from either partial loss of CO₂ by degassing during differentiation of parental magma with very high CO₂ concentrations (see section 4.5) or mixing between degassed and undegassed magmas. The evolved Lac Vert CO₂ values are similar to nepheline-hosted MI from the Nyiragongo summit (~2800-3400 ppm CO₂; Boudoire et al., 2024). The evolved, low-H₂O Nyamulagira Summit MI have much lower CO₂ (250-600 ppm CO₂). These values likely result from more extensive, low-pressure degassing of CO₂ from parental melts during differentiation (Fig. 4).

Positive correlations of F and Cl with K₂O indicate these elements did not degas during differentiation (Fig. S15c-d), becoming concentrated in residual melt, consistent with their higher solubilities. Sulfur, in contrast to F and Cl, does not correlate with increasing K₂O, indicating S was affected by sulfide formation and/or degassing. We assessed potential degassing effects using Sulfur_X (Ding et al., 2023). Modeled degassing paths suggest that while some S is degassed early at high pressure, significant S loss by degassing is only predicted to occur after the majority of CO₂ is degassed (Fig. 4). For Nyiragongo-type MI, only ~400-600 ppm S can be degassed at high pressures compared to ~250-450 ppm S for Nyamulagira-type melts. We note, however, that MI from a given sample likely do not represent a single batch of decompressing magma, and thus modeled degassing curves are more suited for understanding approximate behavior rather than fitting specific datasets. Interestingly, our f_{O_2} estimates for evolved Lac Vert MI based on XANES data are lower than for high-Mg MI (Mugara [01T], NE Tephra [31T]) but are similar to f_{O_2} estimates based on CO/CO₂ measurements of gases from the Nyiragongo lava lake (Sawyer et al. 2008a), suggesting sulfur degassing drives magma towards more reducing conditions.

Sulfide globules occur in the matrix of all samples except Mugara MI (01T) and as inclusions in some olivine phenocrysts, confirming most magmas were sulfide saturated, but it remains unclear to what extent sulfide precipitation modulated the total sulfur budget. To assess potential effects of sulfide formation, we modeled the sulfur concentration at sulfide saturation (SCSS^T) using PySulfSat (Weiser and Gleeson, 2023; Fig. S13a-b) accounting for speciation using the XANES-measured S⁶⁺/ΣS values (see Supplementary Materials). The SCSS^T models suggest only a small number of primitive Nyiragongo-type MI were sulfide saturated at the time of trapping (n=3 of 19 MI), whereas a much larger proportion of Nyamulagira-type MI were sulfide saturated (n=53 of 81). All of the evolved Lac Vert MI are predicted to be sulfide saturated. Estimates of SCSS^T using fractionation models predict Nyamulagira magmas reach sulfide saturation at ~11 wt% MgO, whereas Nyiragongo magmas reach sulfide saturation at ~9 wt% MgO (Fig. S13c). The SCSS^T model results are consistent with the ubiquitous, large (>5 μm diameter) sulfide globules in matrix glasses in Nyamulagira-type and evolved Lac Vert samples and minor sulfide globules in Nyamulagira-type olivine and clinopyroxene phenocrysts.

4.4 Depths of olivine crystallization and implications for magma plumbing systems

Our MI data can be used to estimate the pressures at which olivine crystallized and trapped inclusions (see Supplementary Materials). We employed MagmaSat (Ghiorso and Gualda, 2015) using VESIcal (Wieser et al., 2021) to calculate pressures because it contains the most compositionally diverse calibration range, including silica-undersaturated, high-CaO compositions – parameters strongly affecting CO₂ solubility (see Supplementary Materials). We also recalculated pressures for bubble-free MI from the 2006 and 1986 flank eruptions at Nyamulagira (Head et al., 2011; 68% of their MI were bubble-free).

The most primitive (>Fo85) and volatile-rich (>8000 ppm CO₂) melt inclusions (Mugara, Kirunga, Nzulu, Kituharu, NE Tephra, Shove) yield saturation pressures corresponding to crystallization depths of 10-18 km beneath the flank cones (Fig. 7a) If MIMiC-modeled CO₂ concentrations of ≤2 wt% CO₂ are more accurate, then primitive magma storage depths beneath flank cones would be deeper (depth: 13-23 km). Our data

overall show a wide range of crystallization depths for high-Mg magmas extending to shallower values. Fluid inclusions in high-Fo (Fo_{86-88}) olivine from two Rushayo chain samples (Louaradi et al., 1994) suggest crystallization depths of 11-33 km. The lower end of the fluid inclusion depths overlaps with our MI depth estimates, and if we use the MIMiC CO_2 estimates, the range of overlap is greater (Fig. S22). In either case, the fluid inclusion data clearly show initial crystallization of olivine occurs at greater depths than indicated by MI. Clinopyroxene barometry has also been applied to Nyiragongo and Nyamulagira lavas (Molendijk et al., 2024; Katme Kaleghetso et al., 2025), and a comparison with those results is discussed in the Supplementary Materials.

For comparison with these results, seismic velocity models from two stations near Nyamulagira and Nyiragongo show a broad low velocity zone from ~18-28 km and a smaller low velocity zone at ~10-15 km attributed to magma storage zones (Mavonga et

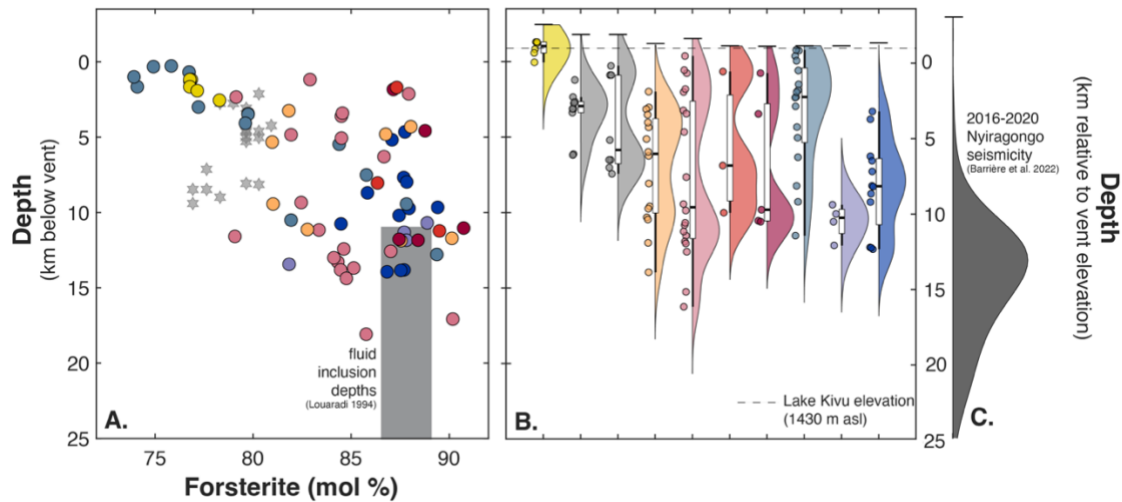


Figure 7. **A.** Olivine crystallization depths calculated from MI vapor saturation pressures versus host olivine compositions. Symbols for MI are the same as in Figs. 2, 4. Gray field indicates depths from fluid inclusions (Louaradi, 1994), using the same pressure-to-depth conversion used for the MI. More information about pressure to depth conversions can be found in the Supplementary Materials. **B.** Depth distributions relative to sea level as points, boxplots, and kernel densities, for each tephra unit. Horizontal lines at the top of each kernel density estimate indicate the vent elevation. The continuous horizontal dotted line indicates the elevation of Lake Kivu. Gray kernel densities represent crystallization depths from tephra erupted in 2006 (left) and 1986 (right) from Nyamulagira (Head et al., 2011) **C.** Depths of seismic events relative to sea level (and as depth below the summit crater of Nyiragongo) detected between 2016 and 2020 in the region from Barrière et al. (2022).

al., 2010). Beneath Nyiragongo, seismic swarms in the 10-14 km depth range are common and have been interpreted as possibly forming during opening of lateral dikes from a magma storage region beneath the volcano (Barrière et al., 2019).

Melt inclusions from the Nyamulagira Summit cone (06T) yield vapor saturation depths <2 km below the summit of the volcano, consistent with a shallow plumbing system feeding Nyamulagira's episodically active lava lake (Fig. 7b). Following a flank eruption in 2011, the lava lake reformed between 2011 and 2015 and again in 2018. Modeling of InSAR data suggested a 3.5-km deep reservoir fed the 2011 flank eruption (Wauthier et al., 2015), which eventually rejuvenated a shallow reservoir in the near summit region, leading to lake reactivation. MI from the 1986 and 2006 flank eruptions, which are also relatively evolved (5.5-6.5 wt% MgO), yield slightly greater depths <10 km depth.

For Lac Vert, primitive Nyamulagira-type MI yield deep (≤ 12 km) storage depths, but more evolved compositions show depths of <5 km. The zoned rim compositions of high-Mg Lac Vert olivine show they re-equilibrated with the shallow-stored, more-evolved host magma. Interaction between deep and shallow plumbing systems is not uncommon at Nyiragongo, as both Mg-rich (Fo₈₅₋₈₆) and more Fe-rich (Fo₇₅) olivine were identified in the 2021 lava flow (Smittarello et al., 2022; Molendijk et al., 2024). Magma stored beneath the main edifice can be transported laterally for significant distances (Wauthier et al., 2012), as shown in the 2021 eruption, where a 25-km long dike propagated southward toward the city of Goma, reaching shallow (500 m) depths below the surface. The high SiO₂ contents in evolved Lac Vert MI, however, make the Nyiragongo lava lake an unlikely source for these melts, suggesting the presence of shallow, evolved reservoirs offset from the main edifice.

4.5 CO₂ concentrations in primary melts

While reconstructed volatile contents show high CO₂ concentrations at time of MI trapping, the melts may have been partially degassed before entrapment. Estimating the original, undegassed CO₂ concentrations of high-Mg melts in this region is challenging, particularly because of the unusual compositions. We used a method based on experimentally determined SiO₂-CO₂ relationships for silica-undersaturated melts

equilibrated with a lherzolite residue (Sun and Dasgupta, 2020). We then compare these estimates to CO_2/Ba ratios for mid-ocean ridge basalts (MORB), ocean island basalts (OIB), and EAR carbonatites. We also consider a method based on combining MI data with $\text{CO}_2/\text{S}^{\text{T}}$ ratios of volcanic gasses (Aiuppa et al., 2021). However, the evolved nature of lavas erupted from the summit regions of both volcanoes makes this method inappropriate for estimating CO_2 concentrations in the high-Mg melts supplied from the mantle.

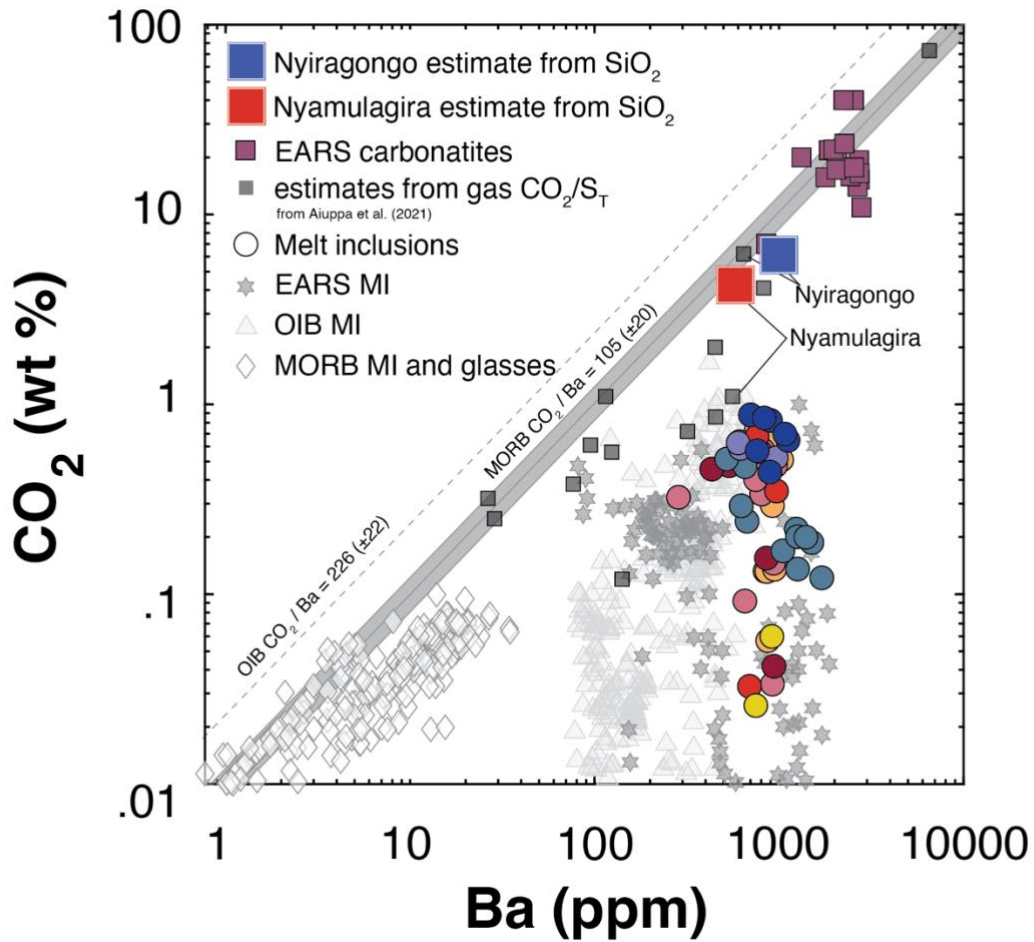


Figure 8. CO_2 versus Ba for our MI compared to other MI from the EARS, OIB, and glasses and MI from global MORB. East African Rift carbonatites are from Innocenzi et al. (2024). Large Blue (Nyiragongo) and red (Nyamulagira) boxes show CO_2 estimates using the relationship between SiO_2 and CO_2 from Sun and Dasgupta (2020). Values estimated by Aiuppa et al. (2021) using volcanic gas CO_2/S ratios are shown as gray boxes. Diagonal lines show Ratios of CO_2/Ba based on global compilations of MORB (Michael and Graham, 2015) and OIB (Sun and Dasgupta 2023).

The sources of primitive melts beneath Nyiragongo and Nyamulagira and the rationale for assuming final equilibration of melts with a lherzolite residue is presented in section 4.6 below.

The use of CO₂/Ba ratios offers a useful perspective on primary CO₂ concentrations because Ba and Nb partition similar to C during mantle melting. For MORB, the CO₂/Ba ratio determined from a global compilation is 105±9 (expressed in ppm/ppm; Michael and Graham, 2015). Interestingly, the CO₂/Ba ratios of carbonatite lavas from the western branch of the EARS (Fig. 8), while variable, show an average CO₂/Ba of 97, suggesting incipient melting of carbonated peridotite generating carbonatitic melts may not appreciably fractionate CO₂ from Ba compared to MORB values. Given the similarity of CO₂/Ba in these disparate magma types, which bracket the Ba concentrations of Nyiragongo and Nyamulagira magmas, we apply a CO₂/Ba ratio of 105±20 to our MI median Ba contents (980 and 580 ppm) to estimate primary melt CO₂ values of 7.8-11.0 wt% (Nyiragongo) and 6.8-9.9 wt% CO₂ (Nyamulagira). Recent work by Sun and Dasgupta (2023) suggests higher CO₂/Ba (226±22) for OIB magmas, which if applied to Nyiragongo and Nyamulagira data, would yield much higher initial CO₂. Given the range of estimates from the different methods, we prefer the SiO₂-calculated values of 6.0±2.5 wt% CO₂ (Nyiragongo) and 4.4±2.5 wt% CO₂ (Nyamulagira) as conservative estimates for primary CO₂ values because they are based on major element composition and equilibration with lherzolite (see section 4.6) rather than relying on CO₂/Ba ratios of magmas with potentially different types of sources.

Magmatic CO₂ concentrations for a range of oceanic island and continental rift volcanoes, including Nyiragongo and Nyamulagira, have also been estimated by assuming CO₂/S^T in volcanic gases represent total degassing of magma rising from depth (Aiuppa et al., 2021). With this assumption, the CO₂/S^T average for a given volcano is multiplied by the S concentration in MI, which are interpreted to represent the undegassed S content of the magma. However, magmas erupted from the summit lava lakes at both Nyiragongo and Nyamulagira are relatively evolved in composition (Figs. 6, S17), and are fed from crustal reservoirs where magma undergoes fractional crystallization (e.g. Molendijk et al., 2024) and possible loss of gas, making this method inappropriate for estimating CO₂ concentrations in primitive, high-Mg magmas.

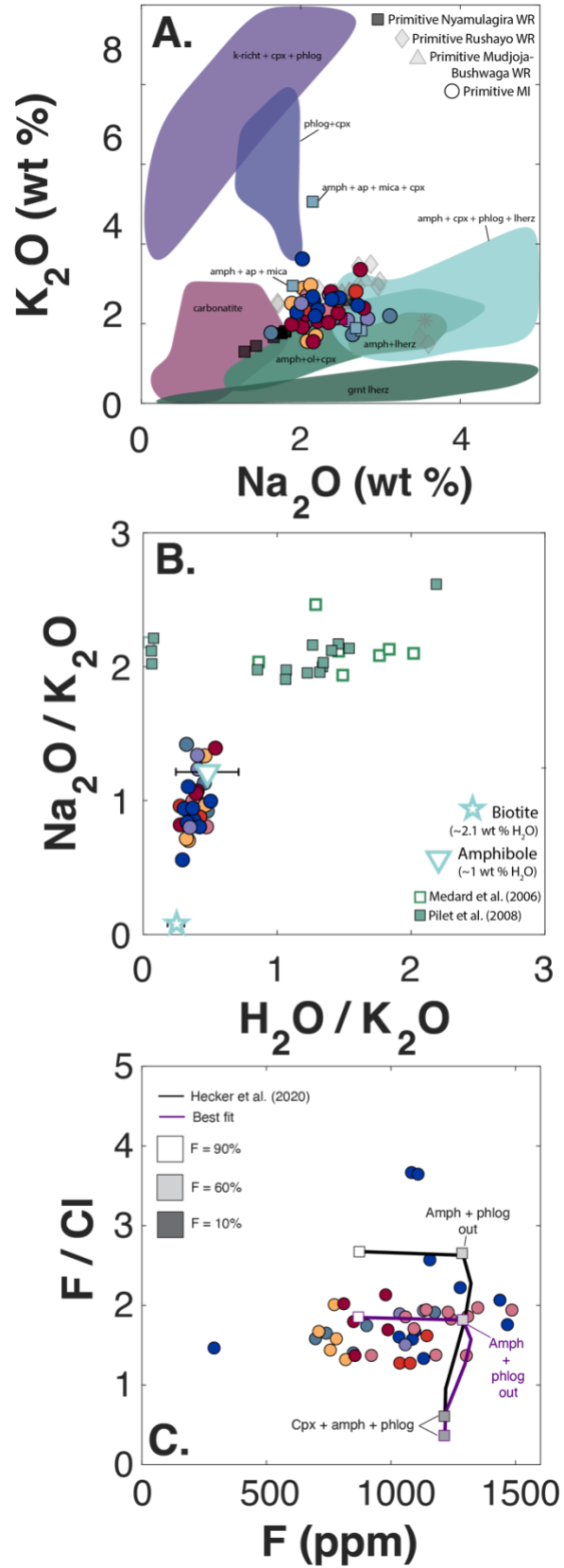
Volcanic gases analyzed at Nyiragongo during persistent lava lake activity typically have molar $\text{CO}_2/\text{S}^{\text{T}}$ ratios of 5-10 (mass ratios of 7-14; Sawyer et al., 2008a; Bobrowski et al., 2017a), with a few higher values up to ~20-30 (molar; Boudoire et al., 2022). The cause of higher values is uncertain, and they may represent a greater contribution of fumarolic and diffuse degassing in the crater region to the plume (Bobrowski et al., 2017b). Lava lake magma at Nyiragongo is relatively evolved, with ~4% MgO and 5% K_2O . Our MI data and results of SCSS^T modeling (Figs. 5, S15) suggest ~1000-1500 ppm S in these evolved melts. Combined with the $\text{CO}_2/\text{S}^{\text{T}}$ mass ratios above, this yields an estimate of 1.3 ± 0.3 wt% CO_2 for evolved magmas undergoing conduit convection between a magma reservoir beneath the volcano and the active lava lake (Sawyer et al., 2008a; see their figure 9).

4.6 Magma source regions: mineralogy and melting processes

Experimental and geochemical studies suggest many potassic magmas require non-peridotitic source regions, leading to a model in which metasomatic veins or domains (metasomes) surrounded by peridotite play an important role (Prelević et al., 2024). Metasomes in the lithospheric mantle beneath the EARS are inferred to be compositionally diverse and spatially heterogeneous. In the Western Branch, increasing $\text{Na}_2\text{O}/\text{K}_2\text{O}$ from north to south (Toro Ankole <0.5, Virunga ~1, Rungwe+S. Kivu >1) has been interpreted to result from variable contributions of amphibole, phlogopite, and other phases within metasomes (Rosenthal et al., 2009). Xenoliths and ultramafic nodules containing pyroxene, phlogopite, carbonate, apatite, Ti-magnetite, and titanite have been identified in the Toro Ankole samples (Lloyd et al., 1985; Innocenzi et al., 2024) and may represent metasome lithologies beneath this region.

To assess metasome mineralogy, we compare MI data (Fig. 9a) to experimental partial melts of a variety of amphibole- and phlogopite-bearing mafic and ultramafic compositions. Partial melts from amphibole-bearing experiments with minor biotite or phlogopite (Foley et al., 1999; Grutzner et al., 2023) most closely resemble primitive MI ($\text{Na}_2\text{O}/\text{K}_2\text{O} = 1$). Melts from Foley et al. (1999) show the influence of varying modal abundances of biotite, amphibole, and clinopyroxene, where amphibole-only and amphibole+apatite melts lie at the higher end of $\text{Na}_2\text{O}/\text{K}_2\text{O}$ for our primitive MI and melts

Figure 9. A. Experimental partial melts of various amphibole and/or phlogopite-bearing mafic and ultramafic assemblages (see section 4.7 of Supplementary Materials). Note that the starting materials of Foley et al. (1999) used biotite rather than phlogopite. Also shown are carbonatites from the western Branch of the EARS (Innocenzi et al. 2024), Primitive (>8 wt % MgO) whole-rock samples from Nyamulagira, Rushayo, and Mudjojda-Bushwaga, and our high-Mg MI. **B.** Primitive MI $\text{H}_2\text{O}/\text{K}_2\text{O}$ versus $\text{Na}_2\text{O}/\text{K}_2\text{O}$ compared to experimental partial melts of amphibole-peridotite (Medard et al., 2006), clinopyroxene-bearing hornblendite (Pilet et al., 2008), and amphibole and biotite compositions from the partial melting experiments of Foley et al. (1999) shown in A. The melt compositions in the latter experiments are dominated by high modal melting of amphibole+minor biotite such that the H_2O contents of the experimental melts can be approximated by the amphibole and biotite compositions. The H_2O contents of the experimental amphibole and biotite were estimated based on analyzed compositions of these phases in mantle samples and as megacrysts in which the oxy-component has been accounted for (Richter et al., 2002; Lamb and Popp, 2009). **C.** Primitive MI F/Cl ratios compared to modeled partial melting of amphibole+minor phlogopite-bearing clinopyroxenite (see section 4.7 of Supplementary Materials).



of amphibole+apatite+biotite+ clinopyroxene bracket the lower end. The comparison of primitive MI compositions and partial melting experiments are consistent with a metasome plus wall-rock melting model (Prelević et al., 2024) in which high degree melts of amphibole+clinopyroxene+minor biotite or phlogopite dominate melt sources beneath Nyiragongo and Nyamulagira (for simplicity we use phlogopite hereafter).

Because amphibole and phlogopite contain significant H₂O, F, and Cl, high modal melting of these phases in the metasomes should control the volatile budget of partial melts. We compare H₂O concentrations in MI to H₂O concentrations in amphibole and phlogopite (Fig. 9b) to better assess source minerals and the source of H₂O in the melts. We used major element compositions of amphibole and phlogopite from Foley et al. (1999) and estimate 1 ± 0.5 wt% H₂O for mantle amphibole (Lamb and Popp, 2009) and 2.1 ± 0.5 wt% H₂O for mantle phlogopite (Richter et al., 2002), accounting in both cases for an oxy(Fe³⁺)-component. As seen with Na₂O/K₂O, ratios of H₂O/K₂O in primitive MI more closely align with amphibole compositions but show a coherent trend towards lower Na₂O/K₂O and H₂O/K₂O consistent with a lesser contribution from phlogopite.

To assess whether melting of an amphibole+phlogopite+clinopyroxene metasome can generate halogen concentrations akin to those in our MI, we constructed a simple melting model (Fig. 9c). We simulated non-modal melting assuming proportions of amphibole (based on experimental data) and phlogopite in the residue linearly decrease at each melting step, with both hydrous phases consumed at F=60%. We used a variety of initial halogen concentrations based on mantle amphibole and phlogopite data from Hecker et al. (2020). To best fit F/Cl ratios in MI (~1.8), moderately higher than median Cl in amphibole and phlogopite from global data are required. We conclude that the metasome melting interpretation is feasible, and the consistency of F/Cl ratios in the primitive MI imply hydrous phases in metasomes are entirely melted to form Virunga magmas.

Molendijk et al. (2025) present a detailed melting model that successfully predicts many compositional features of Nyiragongo primitive melts. In contrast to our interpretation, they conclude amphibole is less important than phlogopite. Their model, however, predicts melts with substantially lower Na₂O/K₂O (0.3-0.7; similar to Toro Ankole volcanics) than the values of our primitive MI. While we both agree on the importance of phlogopite in the metasome source, our comparison with experimental data

suggests a more significant role for amphibole in determining the Na₂O, K₂O and H₂O concentrations of primitive melts.

High initial magmatic CO₂ estimated from our data requires a carbonate mineral to also be present in the source, either in the same metasomes or a distinct second metasome type formed by past infiltration of carbonatite melts, or in carbonated peridotite wall-rock surrounding metasomes. The presence of carbonate can also explain the high CaO in Western Branch magmas, as partial melting of the metasome lithologies discussed above typically does not produce melts with high enough CaO. The high degree melts of metasomes are expected to infiltrate surrounding peridotite wall-rock and react with it (Foley, 1992), and thus the CO₂ content may control the final melt SiO₂ (Sun and Dasgupta, 2023). We conclude that the distinctive low SiO₂ content of Nyiragongo magmas and its very high CO₂ fluxes can both be related to a greater role for carbonate in lithospheric mantle in the Nyiragongo source relative to sources for Nyamulagira and other Virunga primitive melts.

4.7 Comparing degassing models to volcanic gas compositions

Volatile emissions from central crater plumes and fumaroles have been measured at both Nyiragongo and Nyamulagira. The large CO₂ flux from Nyiragongo and large SO₂ fluxes from both volcanoes imply large fluxes of magma, consistent with the persistent lava lake activity at Nyiragongo and frequent eruptions and lava lake activity at Nyamulagira. To understand how magma degassing processes relate to volcanic plume compositions, we have modeled vapor compositions during degassing. As changes in volcanic gas composition or fluxes of SO₂ and CO₂ may signal changes in volcanic activity, it is vital to understand what kinds of magma (partially degassed or undegassed) and degassing depths produce current plume compositions.

We modeled vapor compositions in equilibrium with Nyiragongo and Nyamulagira magmas using Sulfur_X (Ding et al., 2023; see Supplementary Materials). Given the lack of silica-undersaturated compositions in the calibration dataset for Sulfur_X, we cautiously interpret these results, as vapor-melt partitioning of S is more poorly constrained. As discussed in sections 4.2 and 4.5 magmas erupted from the summit lava lakes at both Nyiragongo and Nyamulagira are evolved in composition (Figs. 6, S17). Using initial S

concentrations from evolved MI, f_{O_2} values estimated from Fe-XANES measurements, and CO_2 concentrations calculated from CO_2/S_T in volcanic gases (see section 4.5 and Supplementary Materials), we modeled open- and closed-system degassing (Fig. 10). These models simulate the conduit convection and degassing process proposed by Sawyer et al. (2008a) for Nyiragongo, which should also be relevant for periods of lava lake activity at Nyamulagira.

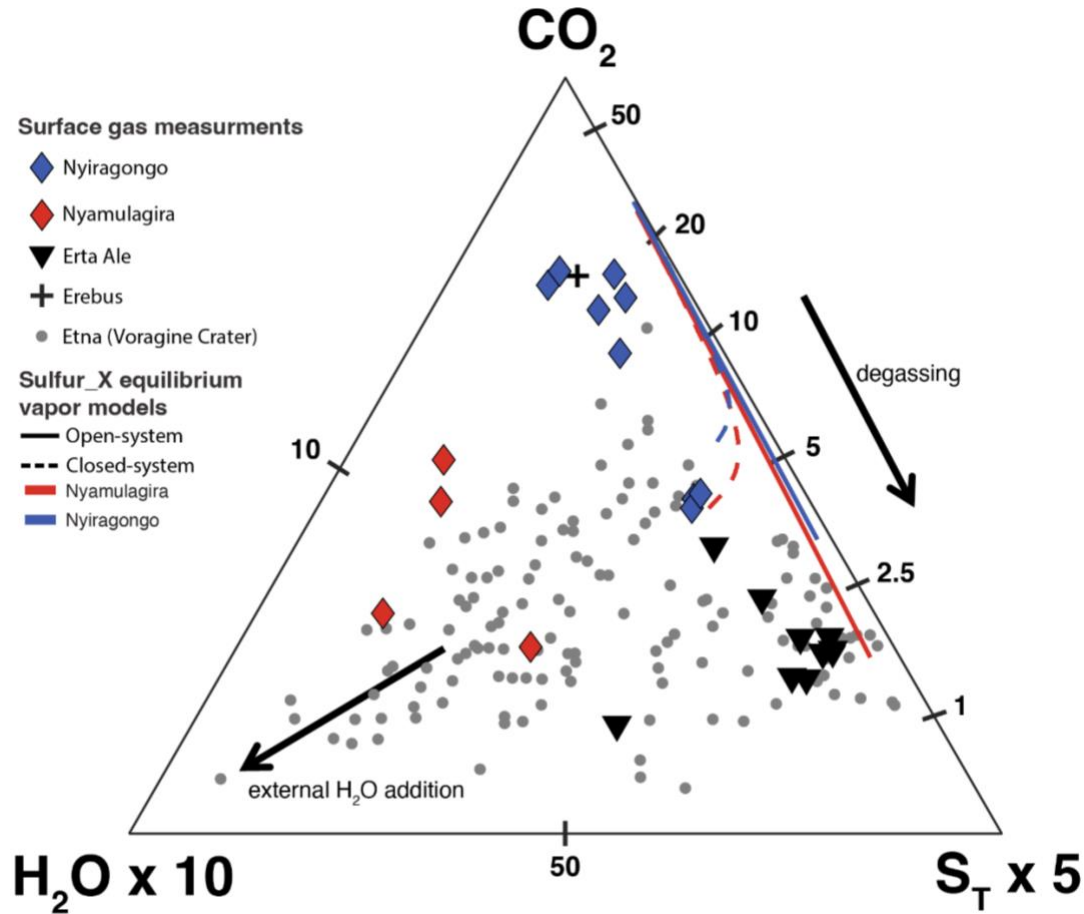


Figure 10. Ternary diagram showing compositions of volcanic gases (in moles) from Nyiragongo (Sawyer et al., 2008a; Boudoire et al., 2022) and Nyamulagira (Bobrowski et al., 2017b; Boudoire et al., 2022) compared to other CO_2 -rich volcanic systems (Erebus: Oppenheimer and Kyle 2008; Etna Voragine Crater: Aiuppa et al., 2016; Erta Ale: de Moor et al. 2013b; Sawyer et al., 2008b). Molar ratios of gas components are shown by labelled tick marks along edges of ternary. Model degassing paths for closed and open systems are shown as solid and dashed curves, respectively. Closed-system degassing paths end at 50 MPa (bottom of curves), whereas open-system paths end at 1 MPa. Initial pressures (tops of curves) are 430 MPa for Nyiragongo and 350 MPa for Nyamulagira.

The model results show the initial gases in equilibrium with melt at depth are relatively CO₂ rich, which is a result of high starting CO₂ contents (1.0-1.3 wt%) we infer for evolved melts. Continued decompression of these melts produces progressively more S-rich gas. During closed-system degassing, the gas composition at low pressure is a nearly identical match to the CO₂/S^T from Nyiragongo's lava lake (molar ratio ~5; Sawyer et al., 2008a; Bobrowski et al., 2017a). The origin of gases with higher CO₂/S^T values at Nyiragongo is unclear. The degassing models suggest they could reflect a larger component of gas released from magma at greater depth during conduit convection, but as previously mentioned, they might instead reflect a greater contribution of CO₂-rich fumarolic and diffuse degassing to the overall plume. For Nyamulagira, no degassing models can reproduce the measured H₂O-rich gas compositions. External H₂O, either meteoric water or high ambient atmospheric humidity, must contaminate the magmatic gas (Boudoire et al., 2022), as has been inferred at Mount Etna's Voragine Crater (Aiuppa et al., 2016). However, the CO₂/S^T ratio of gases measured during the opening stages of Nyamulagira's lava lake activity in 2014 (molar ratio ~4; Bobrowski et al., 2017b) are quite similar to those from Nyiragongo, and can similarly be explained by closed-system degassing and final gas release at very low pressure. Open-system degassing of ascending magma at both volcanoes can produce a much larger spread in CO₂/S^T ratios, and this could explain the lower CO₂/S^T ratios (molar ratio ~0.5) measured at Nyamulagira in 2015 (Bobrowski et al., 2017b).

5. Conclusions

Despite Nyiragongo and Nyamulagira being only 15 km apart, their lava compositions are distinct from one another, with Nyiragongo being strongly silica undersaturated. In our study, the majority of MI and bulk tephra samples analyzed have Nyamulagira-type compositions, similar to lava erupting over the larger Virunga region, making it part of a regionally distinctive magma type. Two of the cones, both proximal to the Nyiragongo edifice, erupted Nyiragongo-type magma, but carry a mixed olivine cargo, including MI with Nyiragongo- and Nyamulagira-type compositions, which requires magma mixing. Using MI volatile data, we estimate a wide range of crystallization depths

for high-Mg melts, with maximum depths of 10-18 km for the most primitive magmas crystallizing beneath the flank vents, and <3km for evolved samples erupted near the Nyamulagira summit. Comparison of our data with degassing models suggests melt S concentrations are affected by degassing (both volcanoes) and sulfide saturation (Nyamulagira-type melts).

We develop degassing models for both volcanoes predicated on a scenario in which evolved, relatively CO₂-rich melts in major magma reservoirs undergo conduit convection and degassing in summit lava lakes. The models successfully predict the compositions of H₂O-poor volcanic gases released from the summit lava lake of Nyiragongo and show that the CO₂/S^T variation in gases could be related to the pressure (depth) at which the gas last equilibrates with magma. Gases from the summit of Nyamulagira are much more H₂O rich and can only be explained by addition of meteoric or atmospheric water, but their CO₂/S^T ratios can also be explained by the degassing model. The high CO₂ fluxes from both volcanoes, one of which (Nyiragongo) has a continuously active lava lake and the other (Nyamulagira), an episodically active one, require relatively high fluxes of primitive melt. Given the growing gas-monitoring capabilities at these volcanoes, future modeling efforts and petrologic constraints can allow for real-time estimates of the depths of degassing magma based on the compositions of gas plumes, if contributions to the plume from fumaroles and diffuse degassing in the craters can be resolved.

Primitive magmas beneath both volcanoes are likely generated in metasomatized lithospheric mantle, and the K₂O and Na₂O concentrations of the melts are best matched by high degree melting of amphibole+clinopyroxene+lesser phlogopite-bearing metasomes. This is a distinctive feature of the Virunga region, as melts further north in the Western EAR are more potassic, requiring more phlogopite in their source, and melts further south are more sodic, requiring amphibole but no phlogopite (Rosenthal et al., 2009). Chlorine and F data for the MI are also consistent with this melting model and a dominant role for amphibole.

The high initial magmatic CO₂ requires carbonate in the source, either in metasomes or surrounding peridotite wall-rock. High degree metasome melts would have infiltrated surrounding peridotite wall-rock and re-equilibrated with the peridotite to some degree. Because SiO₂ concentrations in lherzolite-equilibrated melts are a function of melt

CO₂ (Sun and Dasgupta, 2023), we can use the SiO₂ values at each volcano to estimate primary magma CO₂ concentrations of $\sim 4.4 \pm 2.5$ wt% at Nyamulagira and $\sim 6.0 \pm 2.5$ wt% at Nyiragongo. Thus, both the distinctive low SiO₂ content of Nyiragongo magmas and its very high CO₂ fluxes can be attributed to a greater role for carbonate in the lithospheric mantle of the Nyiragongo source.

1. Bridge

Chapter II examines magmatic processes occurring all the way from melt formation in the lithosphere to the surface release of volcanic gases. This study involved the employment of relatively newly developed techniques (e.g. S-XANES) and the application of recently published geochemical models (e.g. Sulfur_X) to magmatic compositions on the edge of most calibrations. To robustly justify large-scale interpretations made in this paper, a comparatively large amount of supplementary data, information, and discussion is necessary. Chapter III dives deeper into the analytical methods used in Chapter II, allowing researchers to properly replicate the techniques used here. When inputting our data to published models, we needed to rigorously assess which models were most appropriate for our datasets, as improper applications can generate misleading results. While we use melt inclusions in this chapter to constrain magma storage depths, other petrologic methods have been used to estimate pressures and depths of storage. Detailed comparisons with other datasets provide vital context for our results in the broader scientific landscape. With the data and analysis provided in Chapter III, our interpretations in Chapter II can be better utilized by other researchers, and understood within broader scientific contexts.

CHAPTER III: SUPPLEMENTARY MATERIAL FOR: MAGMA SOURCES, CRUSTAL STORAGE DEPTHS, AND DEGASSING OF ALKALIC, CO₂-RICH MAGMAS AT NYIRAGONGO AND NYAMULAGIRA VOLCANOES, DEMOCRATIC REPUBLIC OF THE CONGO

This work was included in an online supplement accompanying publication in Chapter II. Given the many analytical techniques used and modeling methodologies applied in this study, many critical details regarding these methods could not be included in the main text of this short form paper. To properly document this study, we include a detailed supplement that provides enough information for researchers to replicate the study, provides further comparisons of our data to other studies, and dives deeper into the nuances in our interpretations. This chapter includes tephra sampling locations, detailed analytical methodologies, initial conditions and justifications for geochemical models and comparisons to other datasets. Lissie Connors led the writing of this supplement, with editing assistance from Paul Wallace and Kenneth W.W. Sims.

1. Sample localities

Tephra samples in this study (**Table 1; Figure 1**) were collected during a 2015 field expedition (Phillips, 2015). The Mugara cinder cone (01T) is located ~11 km from the summit crater of Nyiragongo, along the N-S trending Mudjoga-Bushwaga chain. Along the Nyamushwa chain, equidistant between Nyiragongo and Mikenno Volcano, sample 31T was collected at an outcrop along Route N2. Given its unknown provenance, we refer to this sample as the NE Tephra. Westward, along the southern extent of the NE-SW trending Rushayo Chain, tephra sample 17T was collected north of Lac Vert, a maar complex with multiple explosive eruptive episodes in the past 2500 years B.P. (Poppe et al., 2016). Tephra sample 39T is located between the Rushayo and Mudjoga-Bushwaga chains along the Lake Kivu shoreline and was collected between Kinungu spatter cone and Kirunga tuff cone, both of which formed in the past 500 years (Poppe et al., 2016). Further west along

Table 1. Summary information for tephra samples used in this study. Magma types are further described in section 4.1 of the main text, and section 3.3 of the supplement.

Sample ID	Locality Name	Classification (from mineralogy and TAS)	Olivine core compositions (mol %Fo)	Magma types (from MI fingerprinting)
DRC01T	Mugara	Olivine basalt	82.6-90.4 (avg = 86.8)	85% Nyiragongo, 15% Nyamulagira
DRC06T	Nyamulagira summit	Tephrite	76.7-78.2 (avg = 77.7)	0% Nyiragongo, 100% Nyamulagira
DRC17T	Lac Vert	Nephelinite	73.6-90.8 (avg = 82.6)	50% Nyiragongo, 50% Nyamulagira
DRC 21T	Nzulu	Alkali basalt	84.1-91 (avg = 88.5)	0% Nyiragongo, 100% Nyamulagira
DRC 22T	Kituharu	Basanite	79.12-90.7 (avg = 85.4)	0% Nyiragongo, 100% Nyamulagira
DRC 23T	Shove	Alkali basalt	79.3-90.3 (avg = 85.6)	0% Nyiragongo, 100% Nyamulagira
DRC31T	NE flank tephra	Alkali basalt	77.2.-90.6 (avg = 86.6)	10% Nyiragongo, 90% Nyamulagira
DRC39T	Kirunga	Olivine basalt	81.8-88.8 (avg = 86.3)	50% Nyiragongo, 50% Nyamulagira

the shores of Lake Kivu, samples 21T and 22T are from the Nzulu (also referred to as Nzulo) and Kituharu tuff cones, respectively. These cones are considered distal cones of Nyamulagira, ~25 km to the north (Smets et al., 2015). Tephra 23T, collected from Shove cone, is closer (~18 km) to Nyamulagira. Tephra sample 06T was collected within the summit crater of Nyamulagira.

2. Analytical methods

To maximize the types of data collected from MI, we followed a sequence of analyses modeled after Rose-Koga et al. (2021; **Fig. S1**). Olivine phenocrysts were picked from lightly crushed tephra samples, and sieved to 250 and 500 μm size fractions. Phenocrysts were mounted on glass slides using clear Crystal Bond 509 $\text{\textcircled{R}}$, then polished within 30 μm of inclusion walls using Silicon carbide sandpaper. Inclusions were examined petrographically (**Fig. S2**), with any partially crystallized or devitrified inclusions removed from the sample suite. In our study, both bubble-bearing and bubble-free inclusions are present. MI exhibit a variety of shapes, with MI from the Nyamulagira summit tephra (06T) exhibiting only smooth-walled MI, whereas other samples dominantly exhibit wrinkle-textured, irregularly shaped MI. Small ($<5\text{ }\mu\text{m}$) sulfide globules are present in some MI, as are cubic spinel crystals. Large ($>20\text{ }\mu\text{m}$ diameter) spinel crystals are interpreted to be co-entrapped with MI.

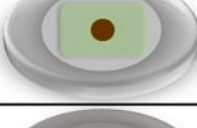
Sample preparation	Analysis	Data product
1. Crush tephra, separate olivine phenocrysts, identify inclusions 	Petrography	Inclusion characteristics (dimensions, shapes, textures, coexisting phases present)
2. Polish sample within ~ 20 micron of inclusion surface 	Raman Spectroscopy	CO_2 density of vapor bubbles
3. Polish sample to expose inclusion 	XANES	Oxidation states of S and Fe in glass
4. Mount sample in indium, coat sample in gold 	SIMS	Volatiles (H_2O , CO_2) in glass
5. Remove gold coat, coat sample in carbon 	EPMA, LA-ICP-MS	Volatiles (S, F, Cl) in glass, major elements in glass, trace elements in glass

Figure 1. Sample preparation workflow for analyzing melt inclusions, modified from Rose-Koga et al. (2021).

Unexposed MI vapor bubbles were analyzed using Raman Spectroscopy at Virginia Tech. After intersecting inclusions, a small subset of samples was analyzed for Fe and S speciation by XANES at Argonne National Laboratory's Advanced Photon Source. Then, MI glasses were mounted in indium, gold-coated, and analyzed for volatiles (H₂O, CO₂, S, F, Cl) using Secondary Ion Mass Spectrometry (SIMS) at Woods Hole Oceanographic Institution. After removing the gold coat and coating samples in carbon, major element concentrations of MI glasses, matrix glasses, and host olivine crystals were analyzed by electron microprobe (EPMA) at the University of Oregon. Time dependent intensity (TDI) corrections were applied for Na, K, Al, Fe, and Si. Trace elements in MI were analyzed using Laser Ablation Inductively Coupled Mass Spectrometry (LA-ICP-MS) at Oregon State University. More detailed descriptions of these analytical methods are described in the following sections.

2.1 Raman Spectroscopy

Raman data (**Table 3**) was collected at Virginia Polytechnic Institute and State University using a JY Horiba LabRam HR (800 mm spectrometer) Raman microprobe, using an 1800 grooves/mm grating and 100x objective. Fitting was conducted using an 8-point linear baseline and a combined Gaussian-Lorentzian (Voigt) fit. Densities are calculated using the densimeter of Lamadrid et al. (2017).

2.2 X-ray Absorption Near-Edge Spectroscopy (XANES)

The redox states of Fe and S play an important role during magma crystallization and degassing. Glasses from rapidly quenched melt inclusions provide a useful opportunity for measuring redox states in-situ using X-ray Absorption Near-Edge Spectroscopy, or XANES. XANES measurements of MI glasses were collected in 2020 at Argonne National Laboratory's Advanced Photon Source, a third-generation synchrotron light source (Sutton et al., 2017). An important consideration when making these measurements is that the obliquity at which the energy travels towards the sample leads to

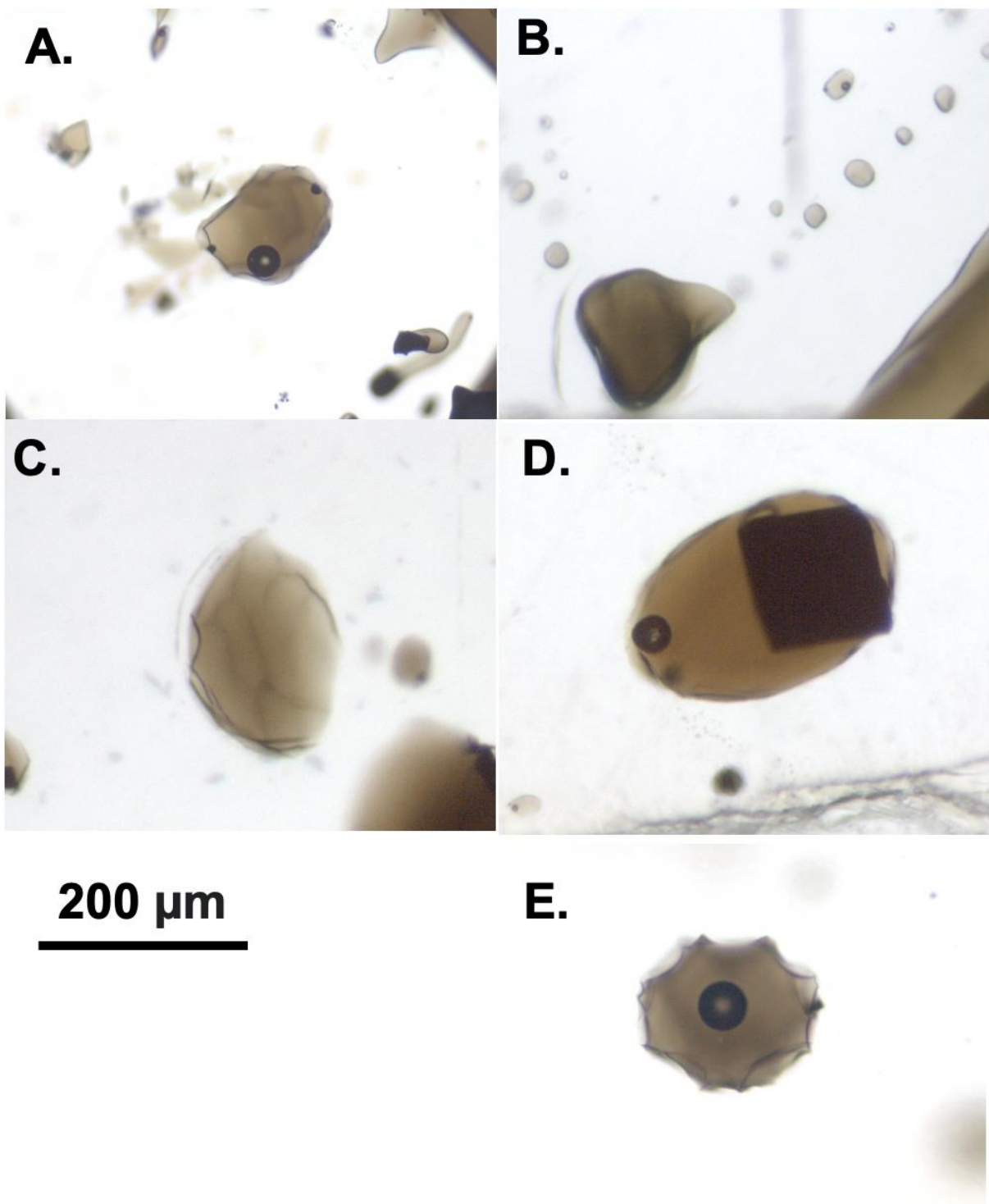


Figure 2. Photomicrographs of melt inclusions. **A.** Wrinkle-textured inclusion, with a vapor bubble and two small sulfide globules. **B.** Smooth-walled, vapor-bubble-free inclusions. **C.** Wrinkle-textured, vapor-bubble-free inclusion. **D.** Inclusion with a vapor bubble and a large co-entrapped Cr-spinel. Note the slight wrinkle texture. **E.** Strongly wrinkle-textured melt inclusion with vapor bubble.

a high likelihood of contamination of the melt inclusion signal by the host olivine crystal, especially considering the scale of melt inclusions, which typically are less than 150 μm in diameter. To minimize contamination by the host crystal, and to maximize target precision, we generated an X-ray map of each sample area by rapidly rastering a $\sim 100 \times 100 \mu\text{m}$ area. After generating the X-ray map, the beam was turned off to minimize beam damage. Analysis positions were then chosen based on regions with the highest X-ray intensity of Ca in S maps, because Ca is present at low concentration in the host crystal.

For Fe XANES, the X-ray signal can penetrate through tens of microns depth below the sample surface, so melt inclusions prepared for Fe XANES were doubly intersected to avoid host-contamination. Because of this, only large inclusions (diameter $> 50 \mu\text{m}$) were chosen for analysis. To minimize beam damage, which can oxidize hydrous glasses during measurement (Cottrell et al., 2018), we decreased the photon flux using high purity aluminum foil filters placed in the beam path, resulting in a beam flux $\sim 1\text{--}6 \times 10^9$ photons/sec. The incident X-ray beam was defocused to a $25 \times 25 \mu\text{m}$ size, avoiding damage to discrete regions. Additionally, scan times were minimized, with a scan step of 0.5 seconds, keeping total scan times under 4 minutes. Silicate glasses, especially those with higher H_2O concentrations, are highly susceptible to beam damage induced by

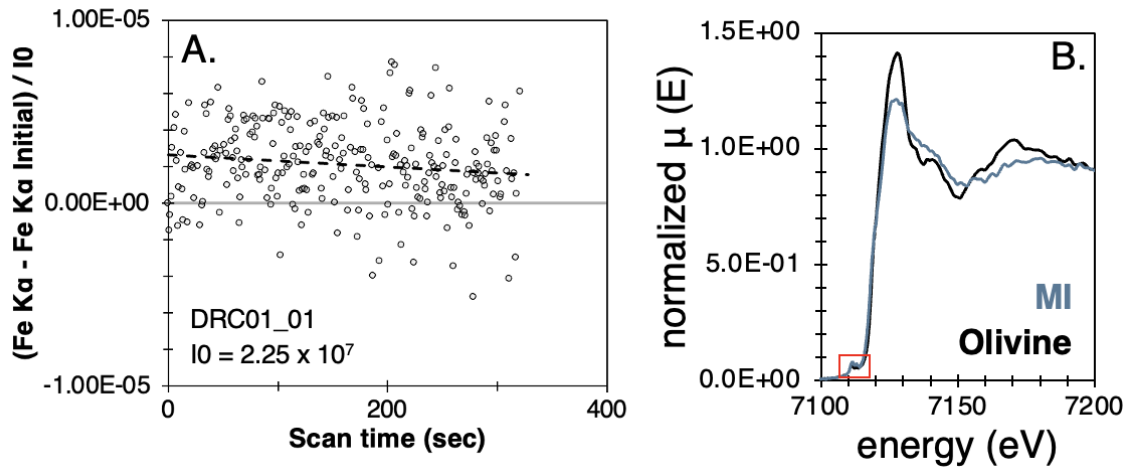


Figure 3. A. Dwell test conducted on MI during 4-minute scan. B. Example spectra of olivine host (black) and MI glass (teal). Pre-edge region is indicated by red square.

radiation exposure. Through conducting dwell tests on natural and experimental glasses with a range of H₂O concentrations, Lerner et al. (2021) found that beam-induced oxidation generally increases linearly over time and corroborated that hydrous glasses are the most susceptible to this type of damage. To assess potential beam damage, we conducted a 360 second continuous scan on an MI with 0.8 wt% H₂O. During this scan, we did not see an increase in the intensity of the second Fe doublet (**Fig. 3**), indicating that the effects of photo-oxidation are likely minimal for our sample suite.

To determine Fe³⁺/ΣFe, measured spectra were normalized to the incident flux (I₀) and fit using the Larix (formerly XAS viewer) program within LARCH software (Newville, 2013). Pre-edge peaks were fit using a Linear+Lorentzian baseline and two gaussians at the Fe²⁺ and Fe³⁺ peaks. Using a similar approach as Cottrell et al. (2009), we calculated centroid energy of the pre-edge Fe doublet, which has been related to standard glasses with known *f*_{O₂} (measured by Mössbauer spectroscopy: Berry et al., 2003; Wilke et al., 2004; Cottrell et al., 2009). To account for measurements in different laboratories (reference glass standards were measured at Brookhaven National Lab, whereas our samples were measured at APS), we applied a correction of +0.356 eV to centroid measurements (the difference in centroid measurements of LW_0 standard reference glass in Cottrell et al., 2009 and 2021, measurements at APS). To calculate Fe³⁺/ΣFe, we used the calibration from Muth and Cottrell (2023), which is an updated calibration from Zhang et al. (2018). We use the corrected centroid value, where *a*₁ = 0.1273, *a*₂ = 0.3616, *a*₃ = 0.1493.

$$\frac{Fe^{3+}}{\Sigma Fe} = a_1 + a_2x + a_3x^2$$

Sulfur XANES measurements were conducted following methodologies outlined in Lerner et al. (2021) during 2020, 2022, and 2023. For S XANES measurements, because S *K*_α X-ray energies are lower than Fe *K*_α, the energy does not propagate as deep as Fe XANES. This means that melt inclusions do not need to be doubly intersected, and therefore smaller inclusions can be analyzed (Wilke et al., 2011). Measurements were conducted in a He-environment, which reduces atmospheric interactions with the X-ray signal. The beam flux ranged from 1.0-1.4 x 10¹⁰, with a defocused beam ranging from 20

x 20 um to 50 x 50 um. As described in Lerner et al. (2021), we measured S K-edge spectra by scanning between 2437-2467 in 2.5 eV steps, and 2467-2487 in 0.01 eV steps.

In natural glasses, sulfur is present as sulfide (S^{2-}) or sulfate (S^{6+}). Similar to Fe XANES, prolonged exposure to the X-ray beam induces damage, in this case photo reducing sulfate (S^{6+}) to sulfite (S^{4+}), lowering the intensity of the S^{6+} peak at ~2480-2482.3 eV. Using the XAS viewer, we assessed beam damage by comparing scan sequences and identifying intergrowths of S^{4+} peaks at ~2476.8-2477.7. When measurements did not exhibit S^{4+} peaks, we merged sample scans to improve the signal clarity.

As with Fe measurements, S XANES measurements were fit using Larix. Flattened spectra were fit using a baseline error function and a gaussian function between 2493 and 2500 eV. Within the S absorption region, five peaks are present (sulfide complexes: 2465-2470 eV, S^{2-} : 2475.3-2477, S^{4+} : 2476.8-2477.7, S^{6+} : 2480-2482.3, sulfur ionization peak: 2483.5-2486). Flattened spectra were then compared to experimental glasses from Jugo et al. (2010), which are interpreted to represent sulfide-only and sulfate-only end members. By considering these two as end members, we can calculate $S^{6+}/\sum S$ using a mixing model. To calculate $S^{6+}/\sum S$, we summed the intensity of the sulfate and sulfide regions, defining the the sum of these two regions as $\sum S^T$. While Jugo et al. (2010) quantifies the relationship of peak intensity to speciation as exponential, the empirical relationship below from Lerner et al. (2021) is also applicable and was used for this study.

$$\frac{S^{6+}}{\sum S} = 0.1733 \times \frac{I(S^{6+})^2}{I(\sum S^T)} + 0.8343 \times \frac{I(S^{6+})}{I(\sum S^T)}$$

Representative spectra used to calculate $S^{6+}/\sum S$ are shown in Figure S4. Because we did S XANES measurements on many more MI than we did Fe XANES measurements, we derived a relationship between $Fe^{3+}/\sum Fe$ and $S^{6+}/\sum S$ to create a general relationship between $S^{6+}/\sum S$ and f_{O_2} that we could apply to our samples. While the speciation of sulfur is a strong function of f_{O_2} , the importance of other parameters such as H_2O concentration and major element composition are not well constrained, especially for the compositions of our MI. Using an approach from Muth and Wallace (2021), we adjusted the constant in the Fe-S redox state versus temperature relationship from O'Neil (2021) to fit our MI data

(**Fig. 4**). Using this relationship to convert $S^{6+}/\Sigma S$ estimates into $Fe^{3+}/\Sigma Fe$ estimates, we then converted the $Fe^{3+}/\Sigma Fe$ estimates into f_{O2} using the formulation of Kress and Carmichael (1991).

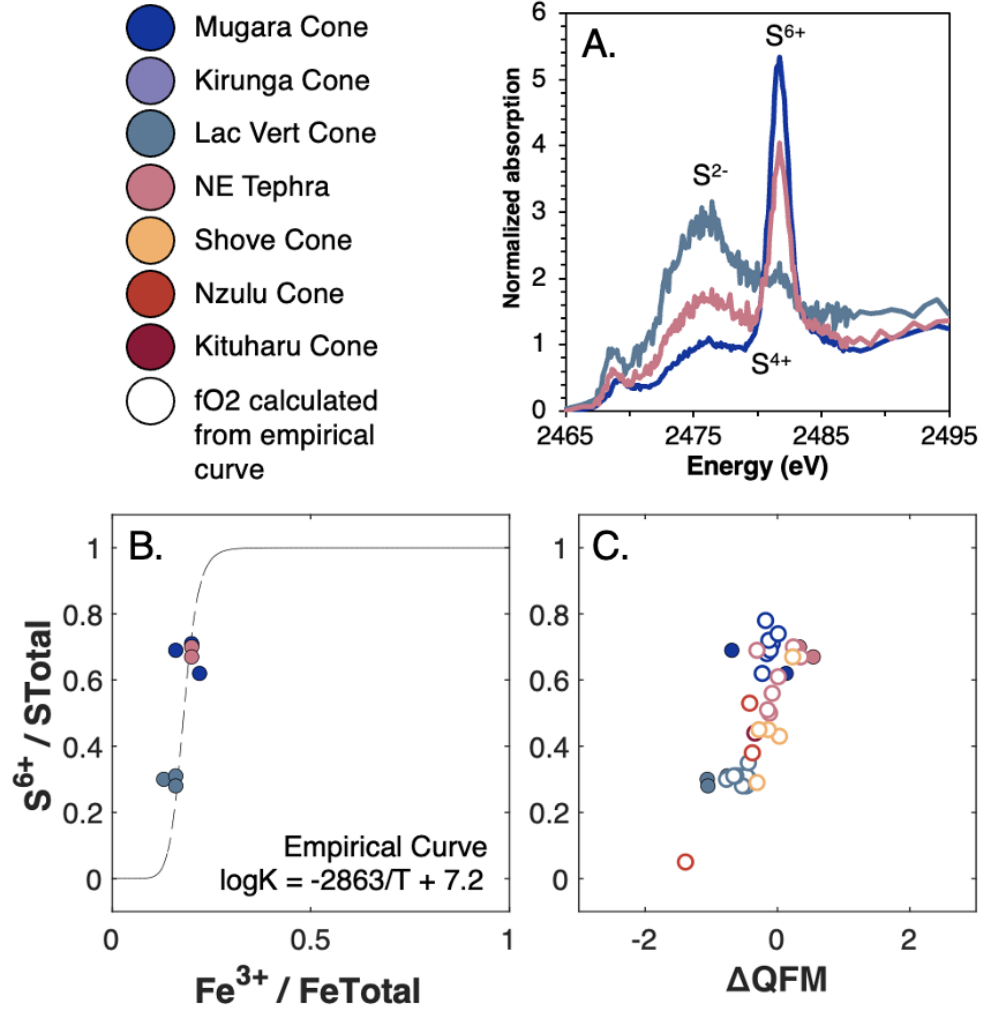


Figure 4. A. Representative S-XANES spectra showing the range of S-speciation measured in MI glasses. B. Melt inclusions for which both Fe and S XANES were measured. The curve shows an empirical relationship between S and Fe speciation modified from the Muth and Wallace (2021) empirical relationship. C. Comparison of calculated f_{O2} with measured S-speciation.

2.3 Secondary Ion Mass Spectrometry (SIMS)

Secondary Ion Mass Spectrometry (SIMS) analyses (**Table 5**) were conducted in 2022 at Woods Hole Oceanographic Institution's Northeast National Ion Microprobe

Facility. All samples were mounted in indium. Melt inclusion glasses were analyzed for CO₂, H₂O, F, Cl, and S using a Cameca IMS1280 with a Cs⁺ beam source.

For volatile measurements, we operated the Cs⁺ beam at 10 kV with a current of ~1 nA. The electron gun was used, with a 50 µm contrast aperture, 600 µm field aperture, and a mass resolving power (MRP) of 6743 FWHM. Each analysis consisted of 300 seconds of sputtering over a 20 x 20 µm area, maintaining a 20 µm raster size during analysis. Count times were 10 seconds for ¹²C, and 4.96 seconds for ¹H, ¹⁹F, ³⁰Si, ³²S, and ³⁵Cl. Wait times were 2.96 seconds for ¹²C, ¹H, ³⁰Si, ³⁵Cl, and 2 seconds for ¹⁹F, and ³²S. Standards (Table S4) were run at the beginning of the weeklong session. These standards comprised of Herasil (background), Suprasil (background), synthetic forsterite (background), and a suite of basaltic glasses: (519-4-1 [CO₂ H₂O, F, S, Cl], D51-3 [CO₂, H₂O, S, F, Cl], 1654-3 [CO₂, H₂O S, F, Cl], 46D [CO₂, H₂O, F, S], 6001 [S, Cl], D52-5 [CO₂, H₂O, S, F, Cl], D30-1 [CO₂, H₂O, F, S, Cl], NS-1 [CO₂], JD17H [H₂O]. Standards of Suprasil glass®, ALV-519-4-1, and VG-2 were embedded in each sample mount and analyzed as secondary standards between every ~25 unknown analyses.

2.4 Electron microprobe analysis (EPMA)

Analyses on MI glasses, matrix glasses, and olivine hosts (**Table 8**) were conducted during 2023 using a Cameca SX100 Electron Microprobe at the Center for Advanced Materials Characterization in Oregon (CAMCOR) at the University of Oregon. For each MI, when size was larger than 25 µm, multiple point analyses were taken and then averaged to account for chemical variability that can be present in MI (e.g. Newcombe et al., 2014), with a maximum of four analyses on a single MI. At least two analyses of olivine hosts were collected within 50 µm of each melt inclusion. When MI had adhering matrix glass, a matrix glass analysis was acquired.

Glass analyses for Si, Na, K, Al, and Fe were run using an accelerating voltage of 15 kV, beam current of 10 nA, and beam size of 8 µm. Analyses for Mg, Ca, Mn, S, Cl, Ti, and P were run using a beam current of 50 nA, and the same voltage and beam size. Counting times were 26 seconds for K, 35 seconds for Mn, 40 seconds for Na, Ca, and Cl, 50 seconds for Si, Al, Fe, Mg, and 60 seconds S, Ti, P. To calculate major element

concentrations in glasses, we used synthetic TiO₂ (for Ti), MnO (for Mn), NBS K-411 mineral glass (for Mg, Ca, and Si), Ca₁₀(PO₄)₆Cl₂ (halogen corrected, for P and Cl), nepheline (for Na and Al), orthoclase (for K), magnetite (for Fe), and pyrite (for S) standards. Time Dependent Intensities were corrected in Probe for Windows software for Na, Si, Al, and K. Through repeated analyses of standards (**Table 7**) during the session, we calculate relative standard errors of 0.1 % for TiO₂, MnO, CaO, and S, and MgO; 0.2 % for SiO₂; 0.3 % for FeO, K₂O, Al₂O₃, and P₂O₅; 0.6 % for Na₂O, and 1.2 % for Cl.

Analyses of olivine were done using an accelerating voltage of 15 kV, beam current of 30 nA, and focused 1 μ m beam. Counting times were 45 seconds for Ni and Ca, 50 seconds for Fe and Si, 55 seconds for Mn, 80 seconds for Mg. To calculate major element concentrations in olivine, we used Mg₂SiO₄ (synthetic forsterite) (for Mg and Si), magnetite (For Fe), and synthetic MnO (for Mn) and NiO (for Ni). Through repeated analyses of standards during the session, we calculate relative standard errors of 0.1 % for NiO and MnO, 0.3 % for MgO and FeO and SiO₂.

Accurate measurements of S in volcanic glasses by EPMA relies on knowing the position of the S K_{α} peak in the glass relative to that for the sulfide or sulfate standard that is used (e.g., Wallace and Carmichael, 1994). We estimated wavelength shifts using constraints on S sulfur speciation derived from XANES measurements. We used an average for each cone for which we have XANES data. For cones with no XANES data, we approximated S speciation by using the average for a similar composition (e.g., unmeasured Kirunga compositions were approximated using Mugara S speciation). For DRC01, 39, and 31, we peaked the spectrometer 20 units below pyrite, for DRC 21T, 22T, 23T, we used 14 spectrometer units below pyrite, and for 17T and 06T we used 8 spectrometer units below pyrite.

We measured Cl and S concentrations using both EPMA and SIMS (see next section). For S, the two methods show relatively good agreement, though at higher concentrations, the EPMA values tend to be slightly higher. The largest deviation occurs for the Mugara samples, which show ~200 ppm lower S concentration by SIMS (**Fig. S5**). We chose to use the EPMA measurements for S, as the sensitivity of the analysis to redox state is better constrained, but given how good the agreement is in general, this choice does not influence any of our interpretations.

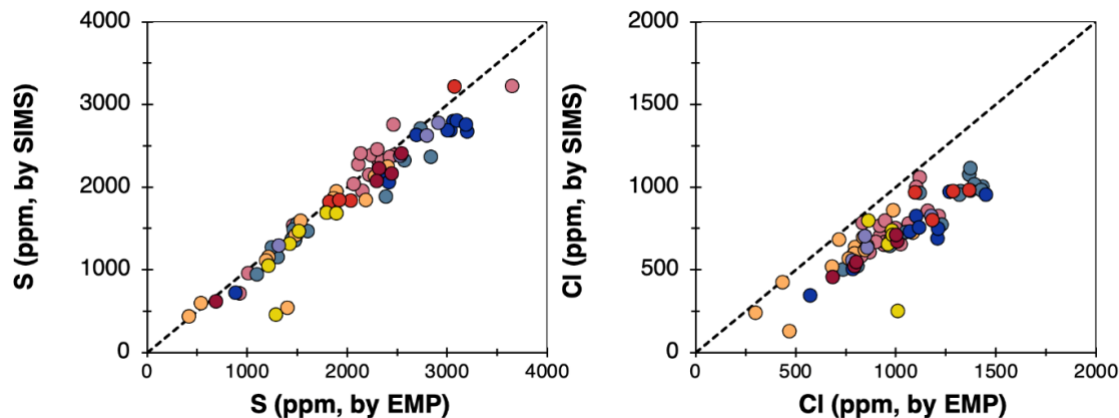


Figure 5. Comparisons of sulfur and chlorine measurements by SIMS versus EPMA for melt inclusions. Dashed lines represent 1:1 relationship.

For Cl measurements, we find that the EPMA measurements systematically show lower Cl concentrations in comparison to SIMS. This is likely due to a difference in standards. Our SIMS calibration includes 6 basaltic glass standards with known Cl concentrations between 45 and 2900 ppm, whereas our EPMA calibration only includes 1 standard of Cl-rich scapolite. We chose to use SIMS measurements for our Cl analyses, as the calibration is more robust.

2.5 Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS)

Trace elements in melt inclusions and matrix glasses (**Table 11**) were measured via Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) using a Thermo Scientific iCAP RQ and photon Machine Analyte G2 193 nm ARF excimer laser at the W.M. Keck Collaboratory for Plasma Spectrometry in the College of Earth, Ocean, and Atmospheric Sciences at Oregon State University in one session in 2023. Melt inclusions were analyzed using a 30 μm spot size, sampling depths of 5 μm , with 86 seconds per analysis. Analyzed trace elements were quantified using calibration standards BCR-2G, BHVO-2G, T1-G, NIST-612. And GSD-1 which were re-analyzed every ~ 10 analyses to ensure reproducibility throughout the session. Raw analyses were processed using LaserTRAM-DB (Lubbers et al., 2021), a dashboard application designed to filter laser ablation signals. We used LaserTRAM-DB to subtract backgrounds from analytical

signals, filter host crystal contaminated signals, calculate detection limits and uncertainties, and apply drift corrections. To calculate concentrations, we used LaserCALC, normalizing concentrations using ^{29}Si as an internal standard.

3. Modeling methods

3.1 Post-entrapment corrections to melt inclusion data

Post-entrapment crystallization of olivine (**Fig. 6**) along the melt-host interface depletes MI of olivine-compatible elements and enriches them in incompatible elements (Danyushevsky and Plechov, 2011). This crystallization also causes a pressure drop in the MI that commonly leads to formation of a vapor bubble that depletes the melt in the MI of volatiles, primarily CO_2 (Moore et al., 2015; Wallace et al., 2015).

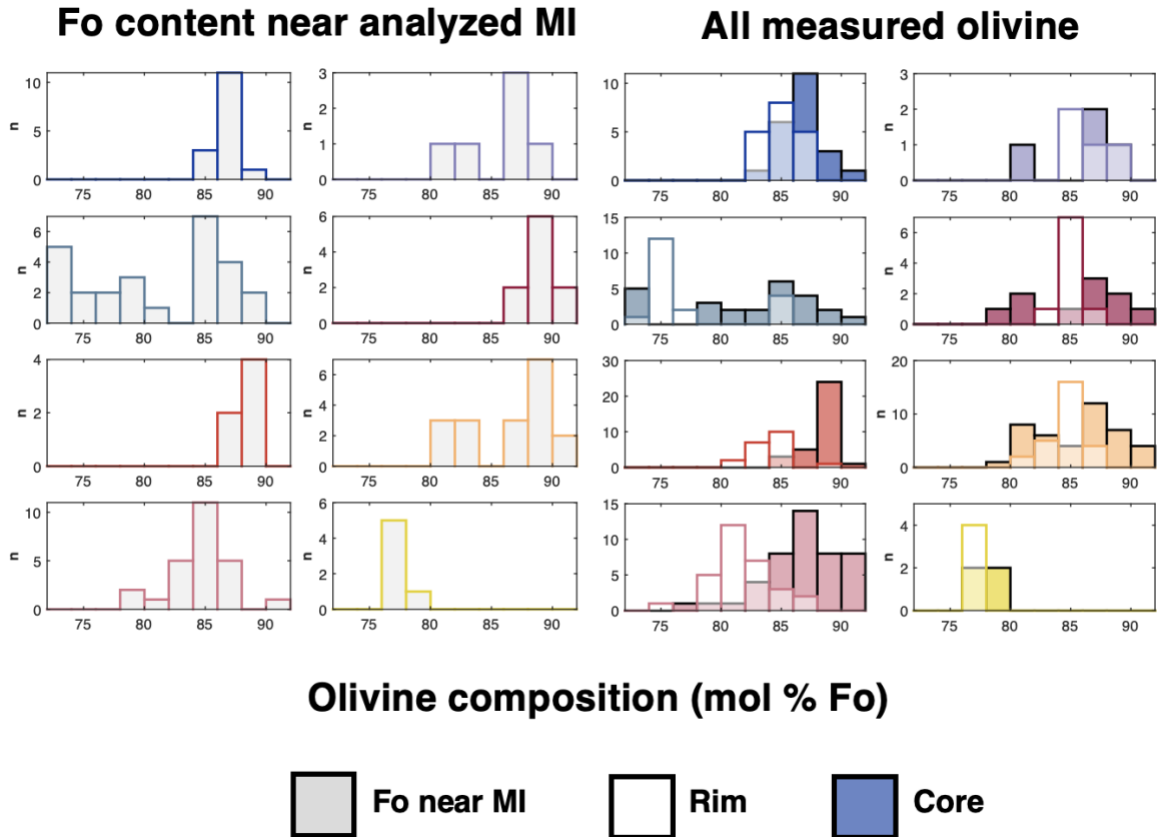


Figure 6. EPMA-measured forsterite content of host olivine phenocrysts near melt inclusions, compared to core and rim analyses of all olivine from each tephra unit.

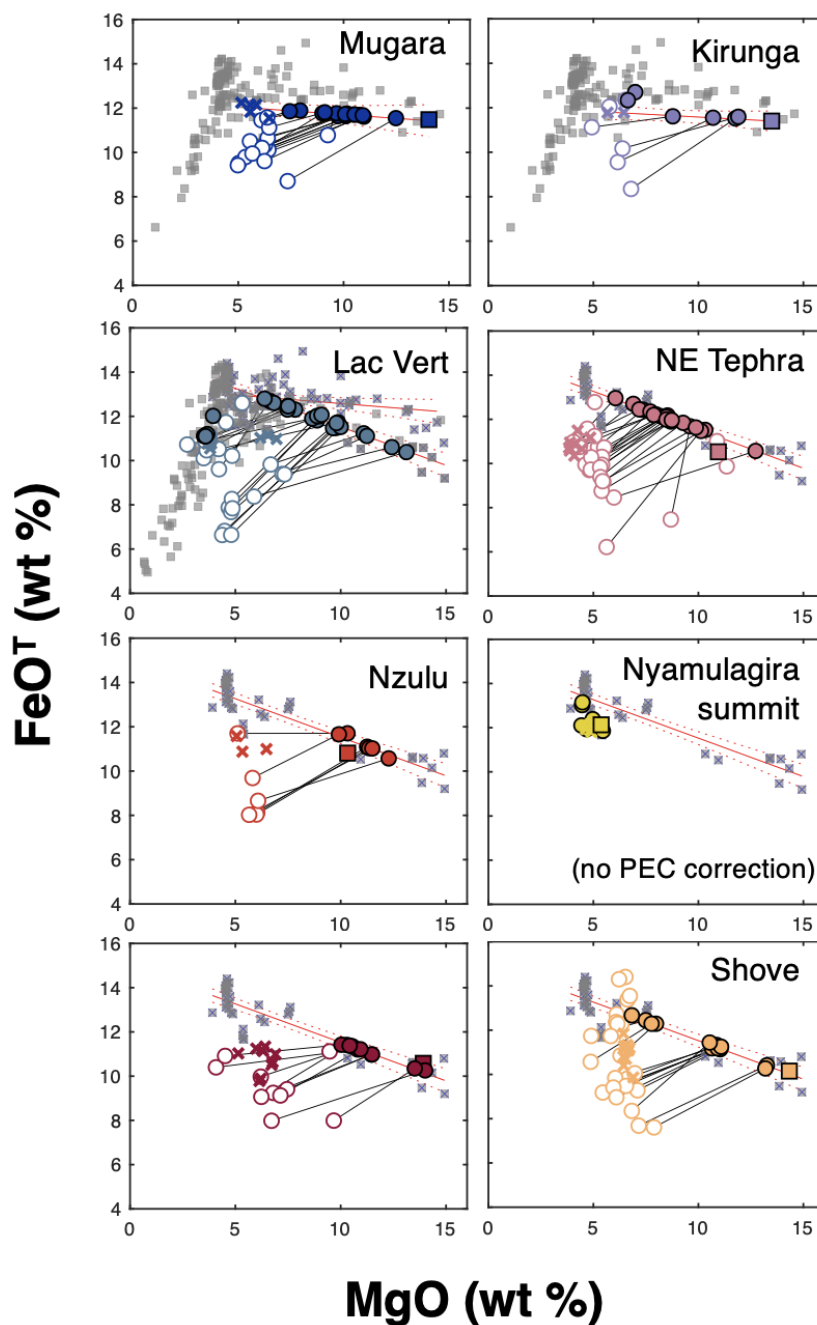


Figure 7. Measured FeOT and MgO in uncorrected inclusions (open circles) and PEC-corrected inclusions (filled circles). Tie lines between the open and filled circles match raw MI measurements to their corrected compositions. Each inclusion FeOT composition was restored to a value based on the linear regression of MgO versus FeOT of an appropriate whole rock array of primitive Nyiragongo or Nyamulagira values. Red lines show linear regressions of primitive whole-rock data, with dotted lines representing the 95% confidence interval of the regression. Whole-rock data are shown by gray squares. Gray squares with x's denote whole rock samples used in the linear regression, with evolved whole rocks from Nyiragongo excluded from the fit. For Lac Vert MI, primitive compositions ($Fo > 85$) were corrected using the regression from Nyamulagira whole rock data, whereas evolved MI from Lac Vert were corrected to the linear regression from Nyiragongo.

In this work, we employed a MI correction procedure in MIMiC (Rasmussen et al., 2020), an open-source python tool. With MIMiC, we used the Fe-Mg partitioning model of Toplis (2005) and iteratively modeled olivine crystallization until the corrected composition of each inclusion overlapped with MgO versus FeO^T trends in whole-rock data for each cone (**Fig. 7**; Table S3). In our models, we use a fixed Fe-speciation. For PEC-corrected inclusions (**Table 10**) the mass % of olivine added/removed from the MI ranged from -1.4 to 24.4 %, with an average of 12.6 mass % olivine added to the MI. For each correction, the slope of the tie lines between raw and corrected MI are determined by the olivine host Fo content as measured within 50 µm of the MI. Three MI analyses at Lac Vert (17T) were corrected for olivine dissolution along the MI-olivine interface, because post-entrapment heating is suggested by higher Fo (reversely zoned) rims. To adequately compare our dataset with previously measured MI at Nyamulagira, we did PEC-corrections using the same methods on MI from tephra from the 2006 and 1986 flank cones (Head et al., 2011), which showed up to 8 mass % of olivine added to the MI. To correct incompatible trace element concentrations for effects of PEC, olivine incompatible elements were multiplied by a dilution factor (**Table 12**), calculated from the ratio of the PEC-corrected K₂O value divided by the raw K₂O analysis.

3.2 Total CO₂ in melt inclusions

The total concentration of CO₂ within MI was determined using a mass balance approach described in Moore and Bodnar (2019), using petrographically estimated volumes of vapor bubble and MI glass, Raman-measured densities of bubble CO₂, SIMS analyses of CO₂ in glass, and glass densities calculated from major element compositions.

$$X_{CO_2}^{inclusion} = \frac{m_{CO_2}^{glass} + m_{CO_2}^{vapor\ bubble}}{m_{total}^{glass} + m_{total}^{vapor\ bubble}}$$

To estimate the volumes of vapor bubbles and MI, both features were measured in two dimensions, and when possible, the third dimension of MI glasses was approximated

by focusing through the depth of the MI with a calibrated optical microscope. Volume calculations assume a spherical vapor bubble:

$$V = \frac{4}{3} \pi r^3$$

and an ellipsoidal MI:

$$V = \frac{4}{3} \pi \times a \times b \times c$$

Recent work from Hanyu et al. (2020) using micro X-ray computed tomography to estimate MI volumes suggests ellipsoidal volume estimates can overestimate MI volumes, leading to underestimations of total CO₂. Furthermore, wrinkled textures and irregular shapes of some MI in our sample suite increase uncertainties in MI volume calculations. Volume reconstructions from DeVitre et al. (2023) found that for irregularly shaped inclusions, optically based volumes increase uncertainty toward both higher and lower vol% bubble estimates when compared to CT-based estimates, with discrepancies increasing as inclusion size increases (Fig S8).

To check the accuracy of our bubble vol% calculation method, we performed X-ray CT scans on two olivine phenocrysts, allowing us to image six MI and their bubbles more accurately. The CT scans were done using a Zeiss Xradia 620 Versa at the University of Oregon's Knight Campus X-Ray imaging facility. We used the results of the CT scans to compare three methods of vapor bubble volume estimation (Fig. S10): (1) 2D estimates from optical microscopy, approximating the c dimension of MI as an average of a and b (2) 3D estimates, using the dimensions of a, b, and c along CT slices, and (3) fully segmenting MI images in 3D Slicer software (Federov et al., 2012). The 2D method systematically underestimates MI volumes in comparison to 3D estimates. This is likely due to oblong MI shapes in our samples, which typically show $b \approx c$. When comparing 3D estimates from dimensions versus segmentations, vapor bubble volume percents vary. Ultimately, the irregular geometry of MI makes it challenging to apply a systematic correction to volume estimations, but we concur with the suggestions of DeVitre et al.

(2023) that polishing MI orthogonally to their longest axis can improve measurements and volume estimations. With these uncertainties in mind, we assume an uncertainty of a ± 1.5 volume % for vapor bubbles, consistent with the differences between the two 3D methods.

For melt inclusions with glass measurements but no Raman-CO₂ density measurement, we assumed a vapor bubble CO₂ density using an average CO₂ density of MI bubbles from the same sample with a similar olivine host composition (within 2 mol %

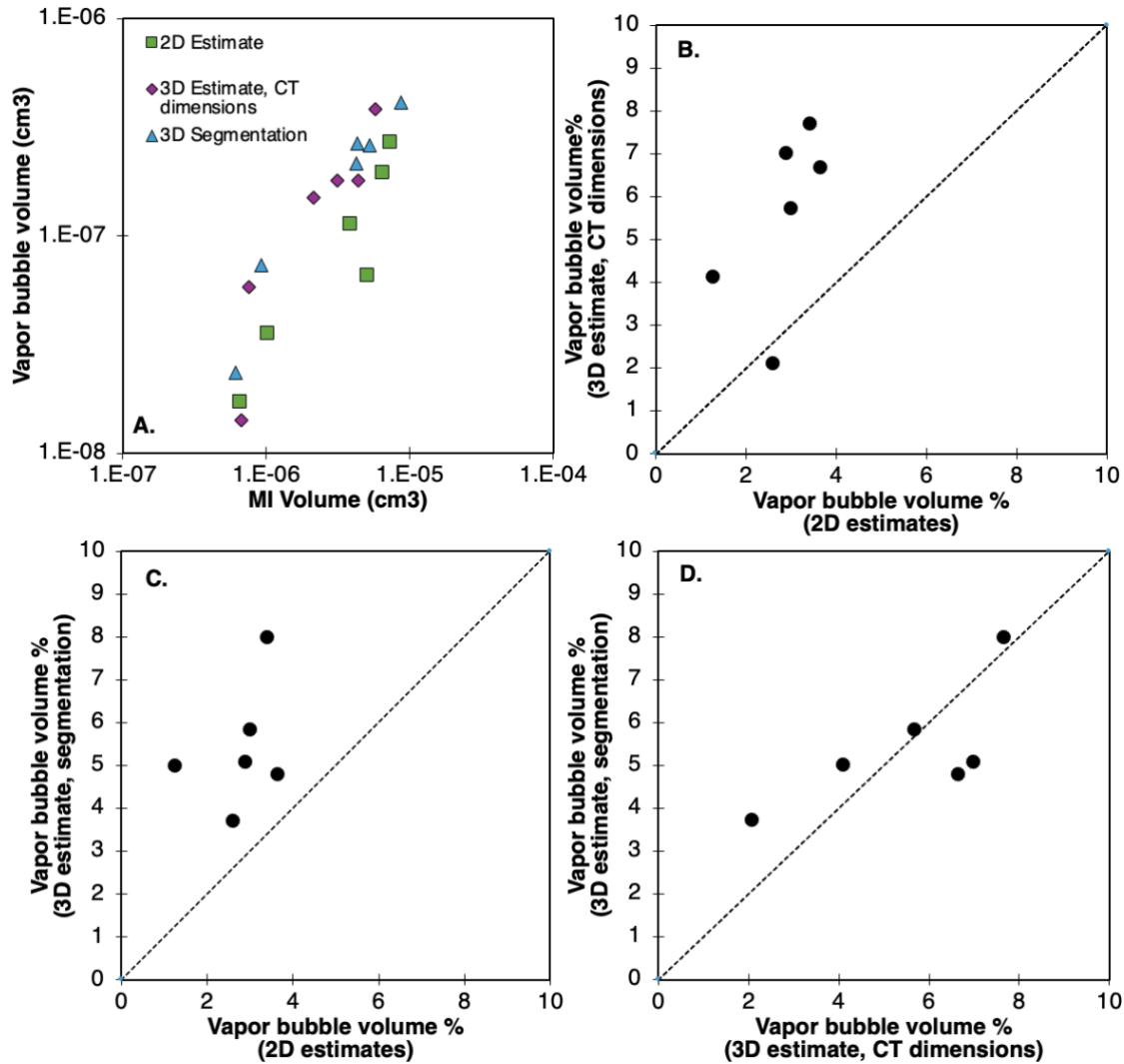


Figure 8. A. Melt inclusion volume estimates from CT scans comparing 2D estimates, 3D estimates, and 3D segmentation estimates. B. Comparison of vapor bubble volume % of 2D estimates versus 3D estimates. C. comparison of 2D estimates versus 3D segmentation estimates. D. Comparison between 3D estimates and 3D segmentation estimates.

we do not make a correction for CO₂ in the bubble and assume glass-only values. Our calculations show that vapor bubbles add as much as 6500 ppm CO₂ to the total MI budget, Fo). This correction was applied to 10 MI in total. As we do not have any Raman measurements of vapor bubbles hosted in low Fo olivine from the Lac Vert Tephra (17T), which equates to as much as 85% of total MI CO₂ being in the vapor bubble. This underscores the importance of accounting for vapor bubble CO₂, which can drastically alter interpretations of magma sources, storage, and evolution. Bubble-free inclusions show systematically lower CO₂ concentrations, highlighting the potential for total volatile underestimation if only bubble-free MI are selected for analysis.

Recent work has illuminated the wealth of mineral phases that can be present along vapor bubble walls, including carbonates and sulfates (Schiavi et al., 2020; Venugopal et al., 2020). To compare the Raman approach with other CO₂-reconstruction approaches, we modeled the behavior of CO₂ during vapor bubble growth using MIMiC (Rasmussen et al., 2020). Using SIMS-measured CO₂ in glass values, estimated vapor bubble volumes, and cooling rates between 5-50°C/sec, we found that MIMiC predicts broadly comparable CO₂ concentrations as those measured using the Raman approach (Fig. 9). Discrepancies

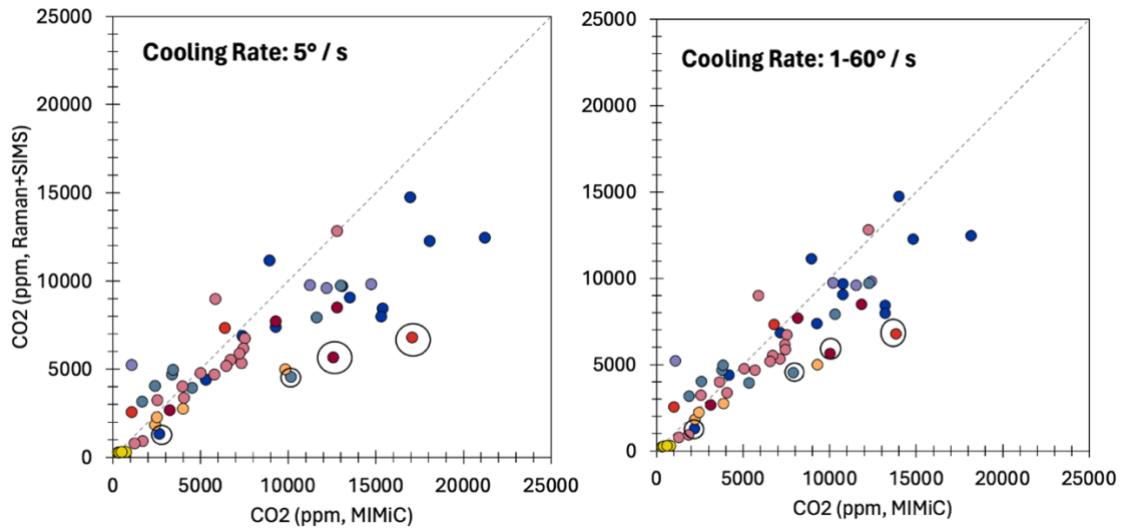


Figure 9. Comparison of restored MI CO₂ contents (vapor bubble+glass) versus CO₂ contents calculated using MIMiC (Rasmussen et al., 2020). Cooling rate at a constant value of 5°C/s yields higher CO₂ concentrations compared to cooling rates calculated by MIMiC using the diameter of MI and host crystal. Circled symbols show MI in which Raman detected carbonate along the vapor bubble wall.

between MIMiC increase at higher CO₂ concentrations (>1 wt %, Raman+glass values), with MIMiC suggesting that MI from the Mugara cone (01T) reach CO₂ concentrations of 2 wt%. We adopt the Raman-based approach for our data, but calculate magma storage depths with both values for comparison (**Fig 21**). Interestingly, when comparing approaches, MI with Raman-detected carbonate phases along vapor bubble walls can be distinguished, as they show some of the largest discrepancies between bubble+glass restoration compared to MIMiC-modeled CO₂ concentrations (**Fig. 9**). Lo Forte et al. (2024) also note this behavior in basanitic MI from Fogo (Canary Islands), further highlighting MIMiC's utility in the absence of direct Raman measurements of vapor bubbles.

3.3 Principal component analysis for fingerprinting magma types

To illustrate the compositional variation of eruptive products in the Virunga Volcanic Province (VVP), Barette et al. (2017) compiled a database of 908 chemical analyses from volcanic centers in the VVP and adopted a multivariate statistics approach for describing compositional differences among volcanic centers. We adopted a similar multivariate statistical approach to assess compositional variability between magmas erupted in close proximity to Nyiragongo's main edifice and magmas erupted in close proximity to Nyamulagira's main edifice. For our dataset, we focused on using whole-rock data from more recent studies. For Nyiragongo, we use samples from studies from 2009 onwards. Given the lower amount of data, we use samples from studies from 1983 onward at Nyamulagira. As lavas from the 1957 eruption of Mugogo (Condomines et al., 2015), located northeast of Nyiragongo and Nyamulagira, are uniquely similar to Nyiragongo we included these whole rock data in our PCA. References for data used in PCA are included below:

- Nyiragongo (n = 287): Chakrabarti et al. (2009); Phillips, 2015; Minissale et al. (2019); Minissale et al. (2022); Moledijk et al. (2023); Molendijk et al. (2024)

- Nyamulagira (n = 67): Caron et al. (1982); Aoki et al. (1984); Aoki et al. (1985); Chakrabarti et al. (2009); Head et al. (2011); Phillips, 2015; Pouclet et al. (2016); Minissale et al. (2019); Minissale et al. (2022)
- Mugogo (n = 3): Condomines et al. (2015)

Before analyzing this dataset, we filtered out samples with anomalously high CaO (>17 wt%) and low SiO₂ (<36wt %). These rocks, typically found in the inner Nyiragongo Crater, are unique in their high degree of crystallinity and presence of matrix calcite (e.g. Demant et al., 1994; Molendijk et al., 2024). These samples, referred to as “altered melilites” by Molendijk et al. (2024), do not represent magmatic compositions and have likely been altered by strong surficial degassing within the crater.

Each variable was normalized by its variance (σ^2) so that the amplitude of each element was considered equally regardless of its overall concentration. The resulting PCA (**Table 14**) shows three components can adequately explain 75% of the variability in the dataset. For our interpretations, we only consider two principal components (**Fig. 5**), which lowers our explained variance to 62%. Our calculated coefficients show that SiO₂, Al₂O₃, MgO, and CaO have the greatest degree of variability in our database, reflected by strongly negative or positive coefficients. Principal component scores of samples from our database illustrate the relatively limited compositional range of samples erupted from Nyamulagira. This lack of diversity may be explained in part by the relatively lower sample size but is also a reflection of the smaller overall range of compositional variation and a more restricted liquid line of descent. In contrast, samples from Nyiragongo show a larger range, reflecting the larger sample size and a wider range of compositions that results from more diversity in differentiation processes (fractionation, olivine accumulation, and leucite and nepheline flotation).

Table 2. Correlation coefficients calculated in principle component analysis

	PC1	PC2
SiO₂	0.77	1.33
TiO₂	0.10	-0.10
Al₂O₃	-0.87	1.08
FeO_T	-0.21	-0.56
MnO	-0.02	-0.01
MgO	1.58	-0.82
CaO	0.27	-1.13
Na₂O	-0.70	0.14
K₂O	-0.72	0.31
P₂O₅	-0.19	-0.16

3.4 Volatile solubility modeling and crystallization depth estimation

Of the many published volatile solubility models, we decided to test MagmaSat (Ghiorso and Gualda, 2015), Iacono-Marziano (Iacono-Marziano et al., 2012), and MafiCH (Allison et al., 2022). These models were chosen because they are calibrated for a wide range of mafic melt composition, including alkalic, silica-undersaturated melts. Carbon dioxide, dissolved in mafic melts as CO_3^{2-} , has a solubility that strongly depends on melt composition, and thus our choice in model is more focused on the accurate constraint of CO_2 solubility. Of the major elements in magmas, Ca^{2+} , Na^+ , and K^+ play the largest role in enhancing solubility, whereas Al^{3+} hinders CO_2 solubility (Allison et al., 2022). The MafiCH model is particularly advantageous because it includes compositions with high concentrations of Na_2O and K_2O , such as those shown in the Lac Vert tephra (17T). Unfortunately, some of our samples fall outside of the Ca^{2+} and Al^{3+} calibration. When only MI with compositions that fall within the major element calibration of MafiCH are considered, resulting volatile saturation pressures show reasonable agreement for most MI with those calculated in MagmaSat and Iacono-Marziano (**Fig. 10**). In addition to having major element compositions outside of the calibration, our samples are less hydrous ($\text{H}_2\text{O} < 1.56 \text{ wt\%}$) than samples used in the MafiCH calibration (Allison et al., 2019: H_2O

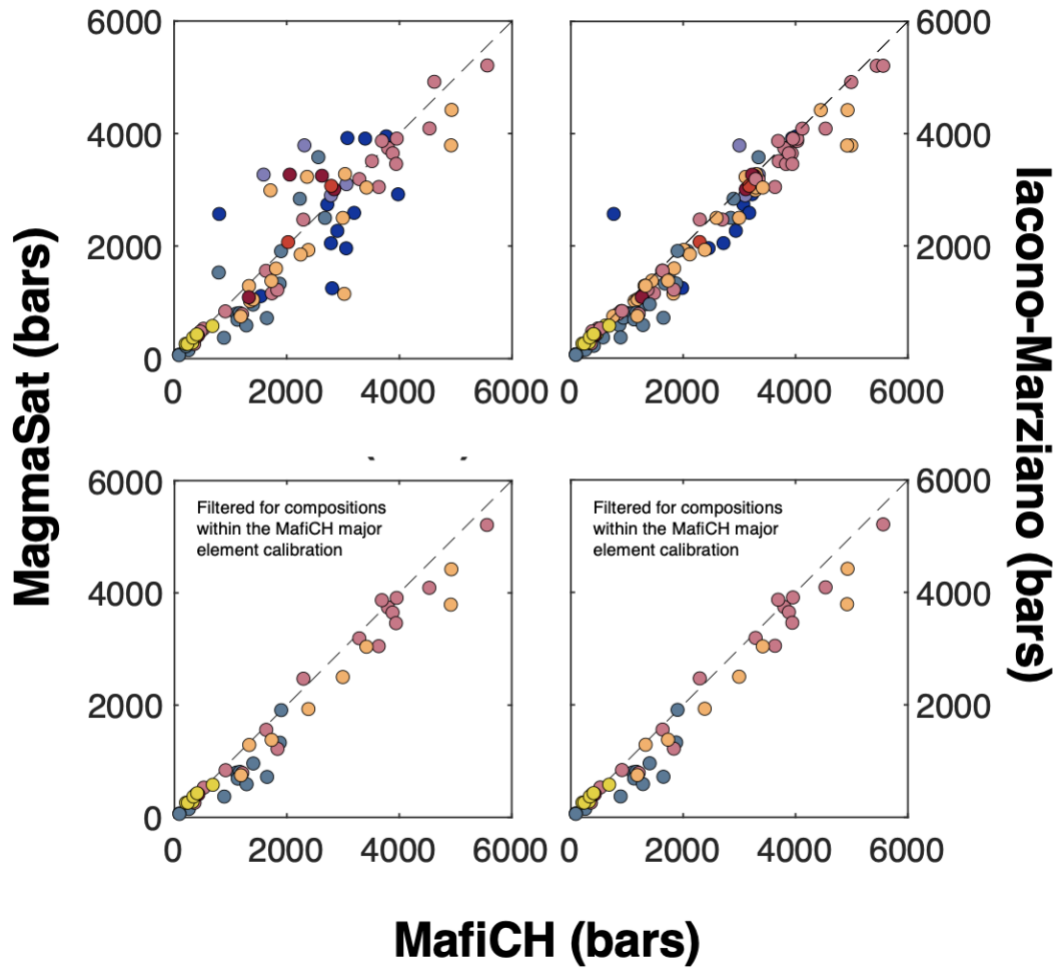


Figure 10. Comparisons of volatile saturation pressures calculated using the MafiCH, MagmaSat, and Iacono-Marziano solubility models. Bottom panels show comparisons between MafiCH, MagmaSat, and Iacono-Marziano, with all MI outside of the MafiCH calibration filtered out.

= 2.12-5.37 wt %). While evolved MI from Lac Vert fall within MafiCH's major element calibration, MafiCH calculates as much as 2x greater storage pressure compared to the MagmaSat and Iacono-Marziano models. For these relatively low-H₂O compositions (0.24-0.37 wt % H₂O; up to 160-2400 ppm CO₂), the differences in pressure estimates likely result from the fact that the MagmaSat and Iacono-Marziano models utilize a formulation in which small amounts of dissolved H₂O increase CO₂ solubility, whereas MafiCH does not. Ultimately, given the number of our MI that fall outside of the MafiCH

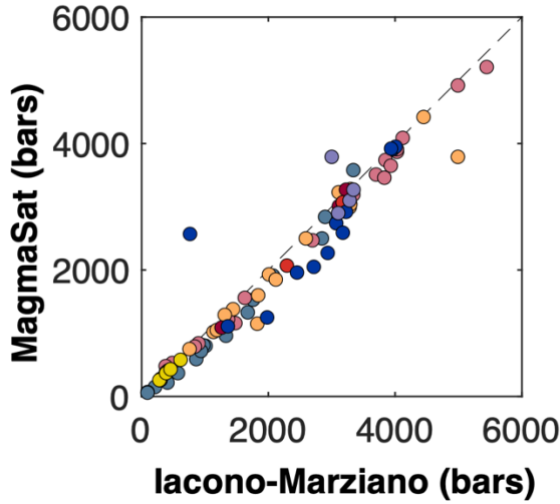


Figure 11. Comparisons of volatile saturation pressures yielded by MagmaSat and Iacono-Marziano solubility models.

calibration, we chose to employ the MagmaSat solubility model, as its calibration included (1) more samples with low H₂O concentrations, (2) a greater range of major element variability, including strongly silica undersaturated compositions, and (3) experiments at high pressure with high dissolved CO₂ concentrations, at wt.% levels.

Volatile saturation pressures calculated in MagmaSat show comparable results to pressures calculated using the Iacono-Marziano model (**Fig. 11**). Although this agreement is encouraging, none of the solubility models is well calibrated for the strongly silica-undersaturated compositions erupted from Nyiragongo, and further experimental work would be required to make improved magma storage estimates from volatile solubility constraints.

Vapor saturation pressures were converted to entrapment depths using a density versus depth relationship derived from Kilauea Volcano based on a polynomial fit of in-situ density estimates from (Ryan et al., 1997), as formulated by Tuohy et al. (2016), where depth is in km, and pressure is in MPa:

$$Depth = (4.578 \times 10^{-8} \times P^3) - (4.151 \times 10^{-5} \times P^2) + (4.652 \times 10^{-2} \times P)$$

In **Figure 7a** in Chapter II, we plot the depths converted from volatile saturation pressures. The depths shown in **Figure 7b** in Chapter II, are relative to sea level. The mass of a large edifice such as Nyamulagira contributes to the pressure-to-depth conversion, so

the depths for MI from the Nyamulagira summit cone shown in **Figure 7b** are relative to the top of the volcano. The flank cones, by contrast, are located at much lower elevations. For example, the Nyamulagira summit cone erupted at ~2940 m above sea level (asl), whereas the distal cones of Nyamulagira (Kituharu and Nzulu) erupted at ~1480 m asl. For the flank cones, the depths for MI in **Figure 7b** are relative to the base elevation of each cone. We use the base of the cone rather than the top (as we did for Nyamulagira) because the cones are relatively small, making negligible contribution to the pressure-to-depth conversion and because magma chambers are sometimes offset from the cones from which they erupt (e.g., Lerner et al., 2020).

3.5 Modeling Sulfur Content at Sulfide Saturation ($SCSS^T$)

To compare measured S concentrations to the amount of dissolved S needed to cause sulfide saturation (SCSS; **Fig. 12a-b**), we used several models in PySulfSat (Wieser and Gleeson, 2023). Multiple models exist for calculating SCSS (Fortin et al, 2015; Smythe et al, 2017; Liu et al, 2021; O'Neill 2021; Blanchard et al, 2021; O'Neill and Mavrogenes 2022; Li and Zhang 2022). We chose to use the Smythe et al. (2017) and O'Neill et al. (2021) models because they are calibrated on the largest experimental datasets and include the effect of H_2O . Sulfur is present as both S^{2-} and S^{6+} in natural silicate melts, with speciation changing rapidly in a relatively narrow f_{O_2} range. The SCSS values calculated using the models above are for dissolved S^{2-} for melts at low f_{O_2} and therefore they underestimate the total S in the melt when applied to melts at intermediate f_{O_2} where S^{6+} is also present. To account for mixed speciation, we use $S^{6+}/\Sigma S$ determined from XANES measurements together with the calculated SCSS to estimate total dissolved S at sulfide saturation ($SCSS^T$). For MI without XANES measurements, we used an average $S^{6+}/\Sigma S$ value for each cone. On average, accounting for S^{6+} results in $SCSS^T$ values that are ~1000 ppm higher than SCSS would be if no S^{6+} was present (i.e., at low f_{O_2}). To approximate sulfide composition, we used partition coefficients from Kiseeva and Wood (2015), which compare closely to the O'Neill (2021) sulfide composition models. For each MI, we used olivine-melt temperatures calculated from Putirka (2008) and vapor saturation pressures calculated in MagmaSat.

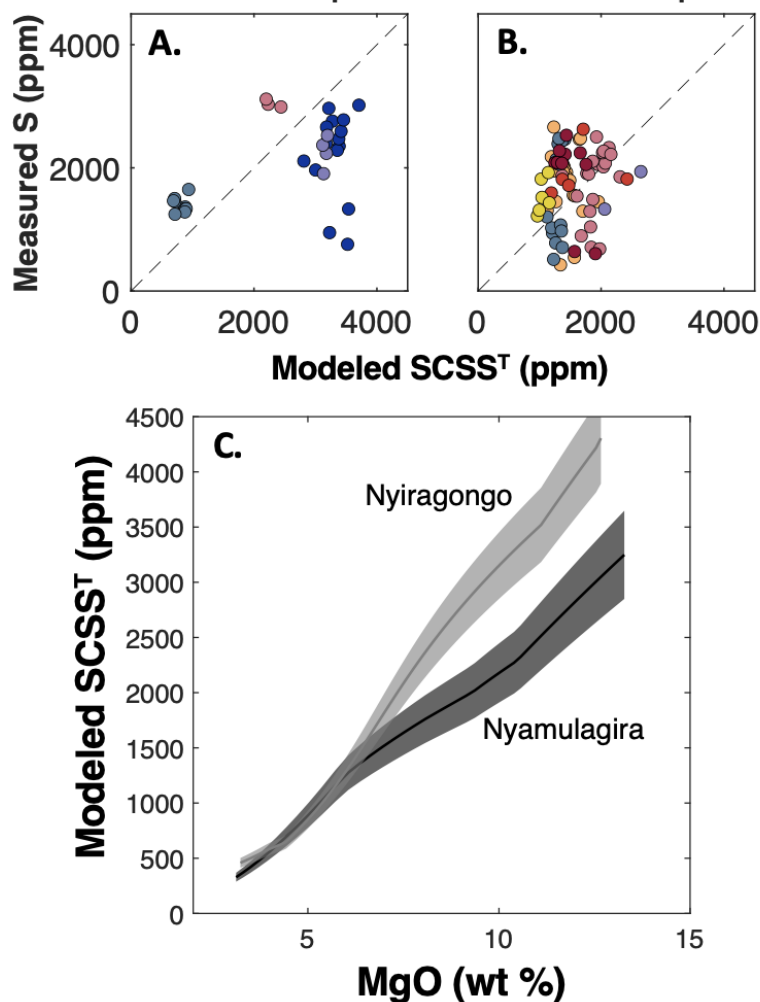


Figure 12. Comparison of measured S contents with SCSST estimates calculated using Smythe et al. (2017) as implemented in PySulfSat. For the calculations, we used $S^{6+}/\Sigma S$ values from the XANES data as described below to estimate the proportions of total S that are present as S^{2-} and S^{6+} . Panel **A** denotes Nyiragongo-type and panel **B** denotes Nyamulagira-type. **C.** Predicted SCSST values along the modeled liquid lines of descent for Nyiragongo and Nyamulagira melts. Fractionation trends for Nyamulagira include both olivine and clinopyroxene, whereas Nyiragongo fractionation trends only include olivine.

When testing the sensitivity of different parameters (e.g. pressure, temperature, H_2O), we found S speciation exhibited the largest control on sulfide saturation, followed by temperature. A greater proportion of sulfide-saturated MI from Nyamulagira is therefore not surprising, as measured ratios of $S^{6+}/\Sigma S$ are slightly lower (median: 0.5) compared to Nyiragongo (median: 0.71), whereas total S contents are comparable for the two types. However, not every MI was analyzed for $S^{6+}/\Sigma S$, so the differences in calculated SCSST

values between Nyiragongo and Nyamulagira MI may be partly the result of how we estimated $S^{6+}/\Sigma S$ for MI not analyzed by XANES.

To assess how $SCSS^T$ varies during fractional crystallization, we also integrated MELTS fractionation models in PySulfSat (**Fig. 12c**). For simplicity, we kept sulfide compositions and sulfur speciation constant throughout the fractionation calculations. While an oversimplification, and not accounting for the evolution of sulfide-compatible trace elements in the melt, to a first order these models suggest that Nyamulagira magmas (which start with about the same dissolved S as primitive Nyiragongo melts) would achieve sulfide saturation at relatively higher MgO concentrations than Nyiragongo. While Nyamulagira whole-rock trends are reasonably approximated through MELTS modeling, as described in the text, our olivine-only liquid line of descent at Nyiragongo does not reproduce whole-rock values with $MgO \leq \sim 7$ wt% (**Fig. 6**), but the model does reasonably well at predicting FeO^T (**Fig. 16**), which is the compositional parameter that most strongly controls sulfide saturation. Consequently, while higher MgO melts at both volcanoes show different $SCSS^T$ estimates, Nyiragongo's predicted $SCSS^T$ values along the fractionation path at lower MgO values are likely to be less accurate.

3.6 Sulfur degassing models using Sulfur_X

We used Sulfur_X to model open- and closed-system degassing of melts. Given that Nyiragongo and Nyamulagira compositions are outside of its calibration range (subalkaline mafic to intermediate melts), we interpret the results with caution. We developed the model calculations to help understand two different processes. The first, shown in **Figure 4**, was to investigate the effects of degassing on the volatile contents of the high-Mg MI. For these models, we used the following starting parameters. For Nyiragongo, we used 1.3 wt% CO_2 , 1 wt% H_2O , and 3100 ppm S, temperature of 1250°C, and f_{O_2} at QFM+0.4. For Nyamulagira, we used 0.9 wt% CO_2 , 1.5 wt% H_2O , and 2500 ppm S, temperature of 1250°C, and f_{O_2} also at QFM+0.4. We employed the Iacono-Marziano H_2O - CO_2 solubility model to calculate pressures of vapor saturation.

The second application of Sulfur_X was to calculate equilibrium vapor compositions for evolved melts that feed the summit lava lakes at each volcano (**Fig. 10**).

The choice of CO₂ and S values for evolved Nyiragongo melts is described in the text (section 4.5) and is 1.3 wt% CO₂ and 1250 ppm S. In addition, we use 1 wt % H₂O (consistent with MI data and degassing models suggesting H₂O remains in the melt until low pressures), 1100°C (consistent with temperatures from evolved MI), and f_{O_2} at QFM, to approximate a more degassed melt. For Nyamulagira we followed a similar methodology, using melt inclusion S for evolved melt based on an average from summit cone MI data (1500 ppm) and the volcanic gas CO₂/S^T mass ratio of ~6.5 (Bobrowski et al., 2017b) to estimate ~1.0 wt% CO₂. We use 1.5 wt % H₂O (consistent with Nyamulagira MI and the degassing relationships outlined above), 1100°C, and f_{O_2} at QFM.

3.7 Modifications to models employing *VolatileCalc*

Both Sulfur_X and MIMiC employ the VolatileCalc solubility model (Newman and Lowenstern, 2002) to estimate volatile saturation pressures. While Sulfur_X offers a choice between the Iacono-Marziano model and VolatileCalc, MIMiC is only formulated using VolatileCalc. We used the Iacono-Marziano solubility model for all Sulfur_X calculations. the VolatileCalc model is limited in its applicability to alkalic compositions because it was formulated using a simplified assumption that the compositional dependence of CO₂ solubility (the π parameter) is linearly related to melt SiO₂ according to the relationship for Hawaiian North Arch glasses with 40-48 wt % SiO₂. In VolatileCalc, the $X^{m_{CO_3^{2-}}}$ reference solubility value is calculated based on this linear relationship of SiO₂ to π for the North Arch samples, as described in equations 7 and 8 of Dixon (1997):

$$\pi = -6.5(Si^{+} + Al^{+}) + 20.17(Ca^{+2} + 0.8K^{+} + 0.7Na^{+} + 0.4Mg^{+2} + 0.4Fe^{+2})$$

$$X^{m_{CO_3^{2-}}}(P_0, T_0) = 8.7 \times 10^{-6} - 1.70 \times 10^{-7} SiO_2 \text{ (wt \%)}$$

Shiskina et al. (2014) suggested that the relationship between SiO₂ and $X^{m_{CO_3^{2-}}}$ is nonlinear, which would make the VolatileCalc model less accurate for compositions with very low SiO₂ and very high π (see **Fig. 13d**). By fitting the glasses from Dixon et al. (1997), which are used to calibrate VolatileCalc, with the same exponential relationship

used in Shishkina (2014) for experiments at 100 MPa, we have generated an exponential relationship between SiO_2 and $X_{\text{mCO}_3}^{2-}$ (**Fig. 13**):

$$X_{\text{mCO}_3}^{2-} = 4.65 \times 10^{-7} \exp(9.05 - 0.17\text{SiO}_2)$$

When this simple alternative formulation is substituted in Sulfur_X and MIMiC, calculated volatile saturation pressures are more comparable to other models such as MagmaSat. We used this modified VolatileCalc formulation for both PEC and CO_2 -in-bubble corrections done in MIMiC.

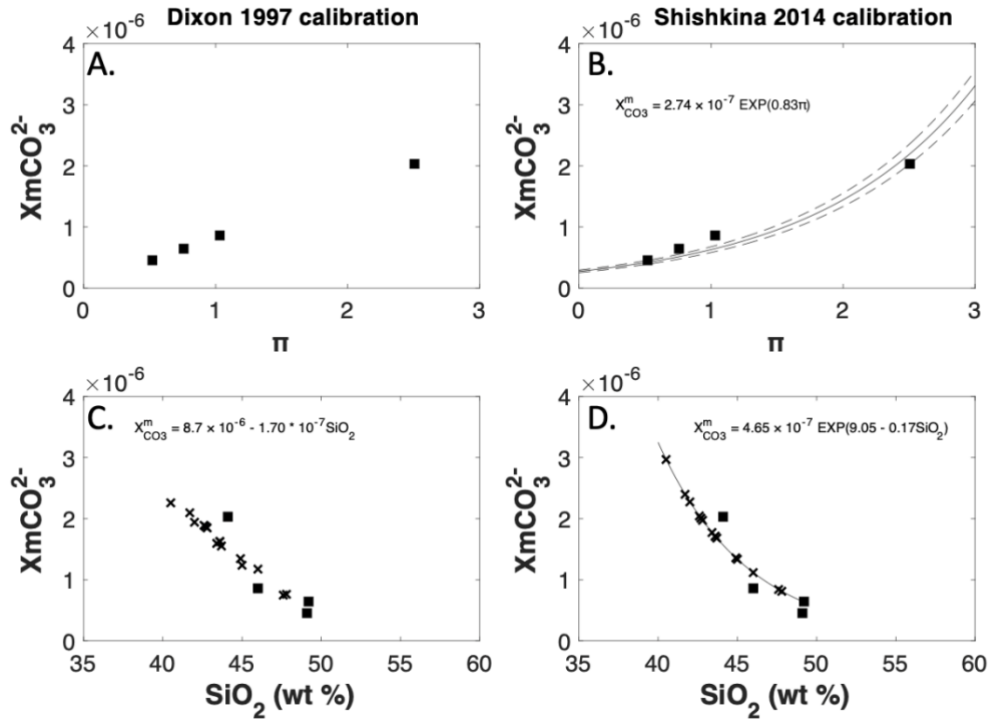


Figure 13. Modification to the VolatileCalc calibration according to the exponential relationship of X_{mCO_3} with π , as found in Shishkina et al. (2014). Black squares indicate solubility experiments from Dixon (1997), whereas x symbols denote data for North Arch Glasses. **A.** Dixon (1997) VolatileCalc calibration. **B.** Dixon (1997) samples with Shishkina exponential fit. **C.** Dixon (1997) calibration with SiO_2 contents of North Arch glasses. **D.** Exponential fit of Dixon (1997) experimental glasses.

4. Supplementary discussion

4.1 Volatile elements

Plots of volatile concentrations in MI compared to K_2O are useful for understanding how magmatic processes modify volatile concentrations (**Fig. 14**). Over the compositional

range of our samples (no leucite crystallization), K₂O is incompatible. The H₂O data falls roughly into two groups. The group with higher concentration (most of the data) shows a weak, scattered positive correlation with K₂O, suggesting H₂O increases during fractional crystallization. The scatter is likely related, at least in part, to minor diffusive losses from MI post-entrapment. The second group, dominated by evolved Lac Vert and Nyamulagira summit cone MI, has low H₂O and shows no relationship to K₂O. As discussed in the text, the low H₂O values likely indicate that the magma had degassed before MI entrapment. The evolved Lac Vert MI have low H₂O and S but contain relatively high CO₂ (1200-2500 ppm). This combination likely results from either partial loss of CO₂ by degassing during

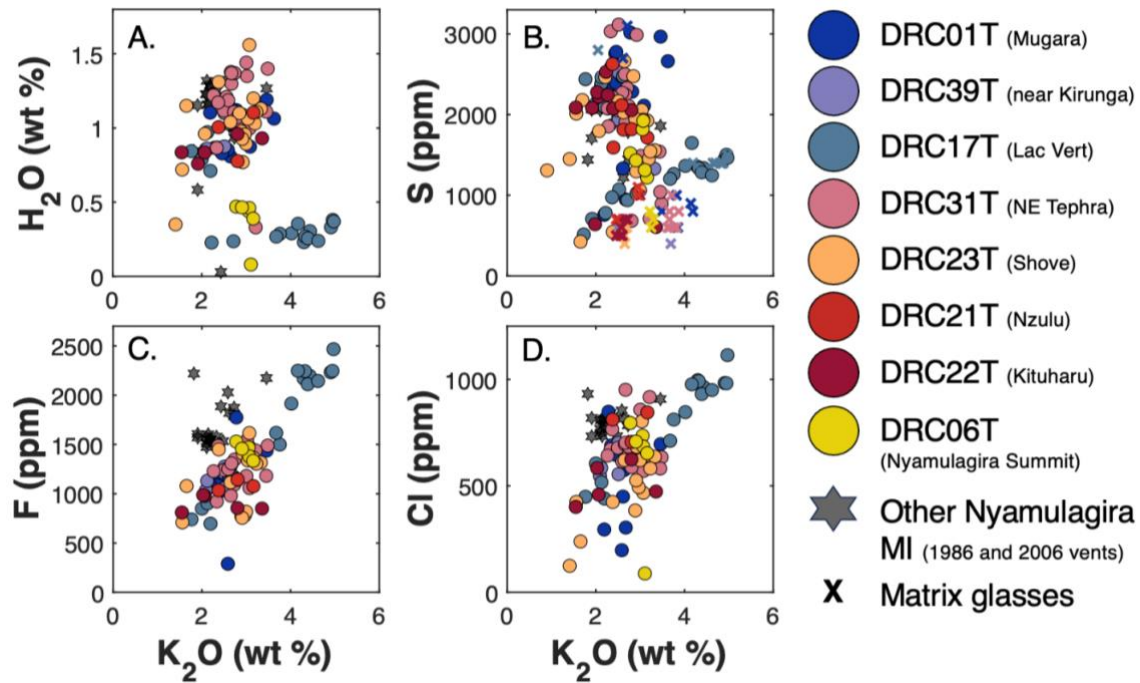


Figure 14. Volatiles in MI glasses versus K₂O, which behaves incompatibly during fractional crystallization. **A.** SIMS-measured H₂O versus K₂O. **B.** EPMA-measured S versus K₂O in MI and matrix glasses. **C.** SIMS-measured F versus K₂O in MI. **D.** SIMS-measured Cl versus K₂O

differentiation of parental magma with very high CO₂ concentrations (see section 4.5) or mixing between degassed and undegassed magmas. The low-H₂O Nyamulagira Summit MI, by contrast, have much lower CO₂ (250-600 ppm CO₂) and could represent melts that lost their H₂O, CO₂, and S through degassing before the MI were trapped. Measured H₂O

concentrations in MI from the Nyiragongo and Nyamulagira flank cones are similar to values found elsewhere in the EARS (**Fig. 15**). In contrast, MI from ocean island volcanoes have a greater range of H₂O concentrations that extends to higher values than found in the EARS.

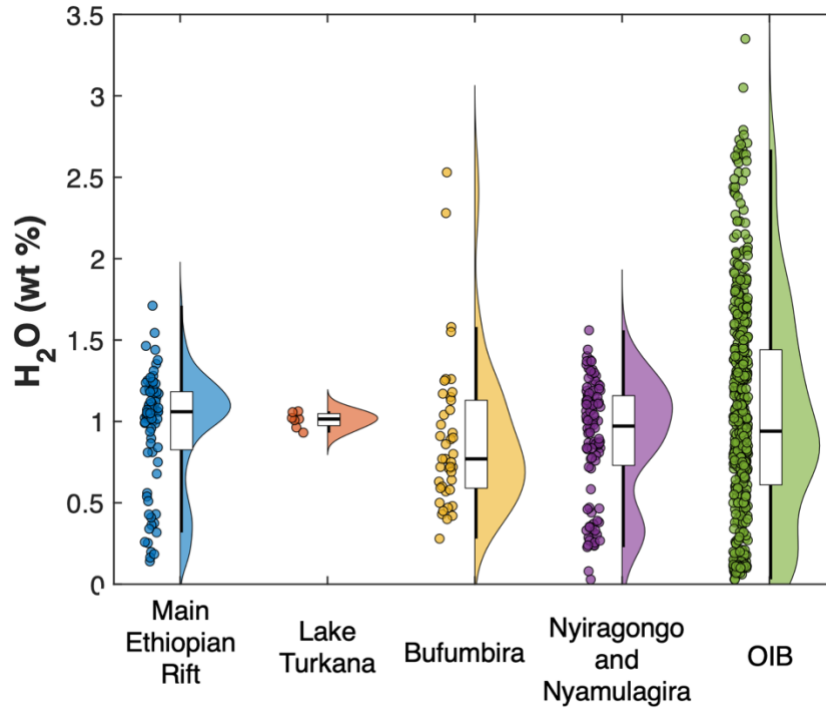


Figure 15. Comparisons of H₂O in MI from localities in the EARS and in ocean island basalts (Main Ethiopian rift: Iddon and Edmonds, 2020; Wong et al., 2023; Lake Turkana: Rooney et al., 2020; Bufumbira: Hudgins et al., 2015; Nyiragongo and Nyamulagira: Head et al., 2011; this study). MI from OIB are from the compilation in DeVitre et al. (2023) and include MI from the Azores, Canary Islands, Galapagos, Sunset Crater (Arizona), and McMurdo Volcanics (Antarctica).

4.2 Major element compositional variations

Variation diagrams for Al₂O₃, CaO, TiO₂, P₂O₅ versus MgO are shown in Chapter II **Figure 6**, and additional diagrams for SiO₂, FeO^T, Na₂O, and K₂O are shown in **Figure 16**. Whole rock, MI, and matrix SiO₂ differ between Nyiragongo and Nyamulagira, with Nyamulagira samples ranging from 42-49 wt%, and Nyiragongo samples ranging from 36-48 wt%. As discussed previously, the FeO^T values of the MI are based on the whole-rock trend that was used for doing the PEC and Fe-correction calculations, so actual values at

the time of trapping would likely show more scatter than what is plotted here. Both Na₂O and K₂O display incompatible behavior during fractional crystallization.

In the figures, purple dashed lines show liquid lines of descent from Molendijk et al. (2024), which were calculated from experimental mineral-melt partition coefficients and modal mineral abundances. The black dashed lines represent best fitting liquid lines of descent of MI and matrix glasses that we modeled using MELTS (Gualda et al., 2012). For Nyiragongo, the MELTS models represent olivine-only fractionation, as this best approximated the compositional trends shown by Nyiragongo-type MI and matrix glasses, which reach high CaO contents (15-17 wt%). We chose an initial melt composition with 12.5 wt% MgO, consistent with the most primitive Nyiragongo MI. Models were run at 450 MPa, with 1 wt % H₂O, from 1250°C to 1000°C. Three models are shown in Figure 6 for parent melts with different initial P₂O₅ concentrations, but other major elements are the same in all models.

For the Nyamulagira parent melt, we used the highest MgO MI compositions from the Kituharu tephra (22T, 14 wt% MgO), with 1.5 wt% H₂O, and we modeled multiphase fractionation from 1250° to 1000°C. The MELTS model most closely approximating whole-rock trends (Chapter II **Fig. 6**, Chapter III **Fig. 17**) involves fractionation of olivine and clinopyroxene with minor Cr-spinel and, at lower MgO, titanomagnetite. While MELTS models predict olivine-only fractionation over a short temperature interval, trends could also be explained by concurrent fractionation of both olivine and clinopyroxene, as noted also by Kaleghetso et al. (2025). petrographic observations of olivine inclusions in clinopyroxene supports simultaneous crystallization of these two phases. Disequilibrium textures of clinopyroxene megacrysts in the Nzulu, Kituharu, NE Tephra, and Shove tephra suggest the larger crystals are xenocrysts or antecrysts, requiring further investigation.

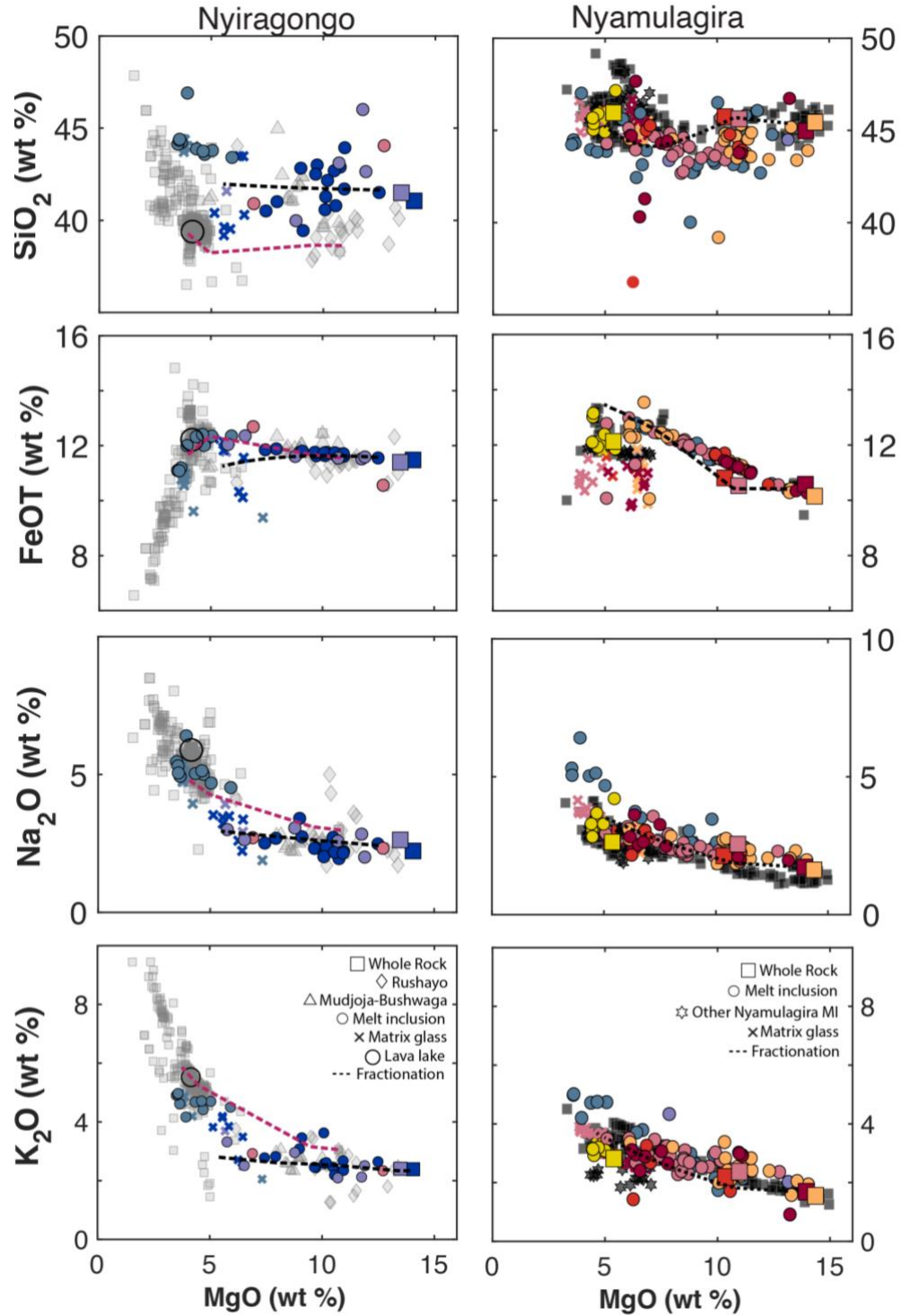


Figure 16. Major element compositions of whole rock, MI, and matrix glasses, separated into Nyamulagira and Nyiragongo types based on principal component fields. Whole-rock data from Caron et al. (1982); Aoki et al. (1983); Aoki et al. (1985); Chakrabarti et al. (2009); Head et al. (2011); Phillips (2015); Minissale et al. (2019); Minissale et al. (2022); Molendijk et al. (2023); Molendijk et al. (2024). Additional Nyamulagira melt inclusion data from Head et al. (2011). Liquid lines of descent from Molendijk et al. (2024) are shown in purple. Modeled MELTS curves approximating MI and matrix glass data are shown in black.

4.3 Trace element compositional variations

To contextualize the trace element signatures of primitive Nyiragongo-type and Nyamulagira-type MI, we constructed spider diagrams (**Fig. 17**) of primitive whole-rock samples from our compilation of literature data ($\text{MgO} > 8 \text{ wt } \%$) to compare with trace element analyses of our primitive MI. Generally, primitive Nyiragongo whole rocks have higher incompatible trace element concentrations relative to Nyamulagira, although the Nyiragongo dataset is much larger ($n = 73$ versus $n = 8$). A striking feature of Nyiragongo whole-rocks is relative depletions in Pb and Hf. Primitive Mugara (01T) MI also have prominent Pb depletions but are not as enriched as most primitive whole-rock samples in the Nyiragongo compilation, consistent with the variations in P shown in Figure 6. Primitive Nyamulagira MI show a range of incompatible trace element concentrations that overlaps entirely with the limited whole-rock data.

Incompatible trace element concentrations are highest in evolved Lac Vert MI (not shown), which is likely a result of extensive fractionational crystallization. In general, MI have higher concentrations of incompatible elements than their bulk tephra host, and matrix glasses have higher concentrations than MI.

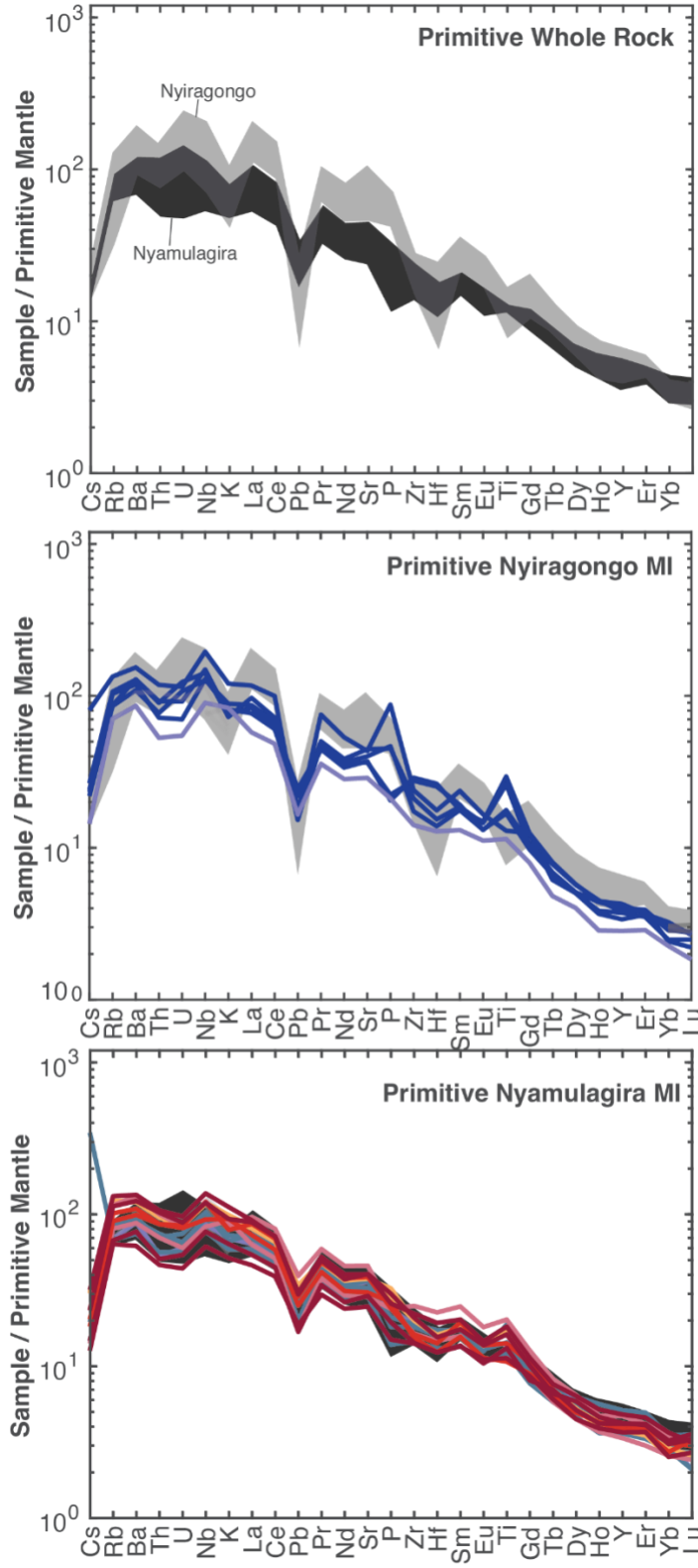


Figure 17. Spider diagrams for primitive (>8 wt % MgO) whole-rock compositions and MI. Top panel shows the range in trace elements for Nyiragongo (gray) and Nyamulagira (black) whole-rock samples. The bottom two panels show primitive MI classified as Nyiragongo- or Nyamulagira-type according to PCA (described in section 3.3 in the supplement and 4.1 in the main text) superimposed on whole-rock data (gray). All samples are normalized to primitive mantle from Sun and McDonough (1989).

4.4 Assessing differing fractionation trends at Nyiragongo and Nyamulagira

Differences in the compositions of Nyiragongo and Nyamulagira magmas have been attributed to differences in both source materials and fractional crystallization histories. Here, we discuss differences in fractional crystallization and liquid lines of descent for the two volcanoes. Past studies have highlighted the important role of olivine and clinopyroxene fractionation in primitive magma evolution at both systems (Aoki et al., 1985; Platz et al., 2004), with olivine, clinopyroxene and melilite playing a significant role at Nyiragongo (Molendijk et al., 2024). For MgO-rich magmas at Nyiragongo, the role of melilite may be variable. Cones from the Mudjoja-Bushwaga chain, including the Mugara tephra (01T), are noticeably melilite poor and clinopyroxene rich. According to experiments from Yoder (1975), the crystallization of melilite in CO₂-saturated magmas is pressure-dependent, with lower pressure systems favoring diopside crystallization. If applicable to Nyiragongo and Nyamulagira, identifying a record of melilite fractionation may imply differences in storage depth. The geochemical signature of melilite versus clinopyroxene fractionation is challenging to identify in whole-rock and MI trends, as they incorporate similar major and trace elements (Minissale et al., 2019; Molendijk et al., 2023). Scandium however more readily partitions into clinopyroxene (Minissale et al., 2019; Molendijk et al., 2023) compared to melilite, and therefore is an effective tracer of

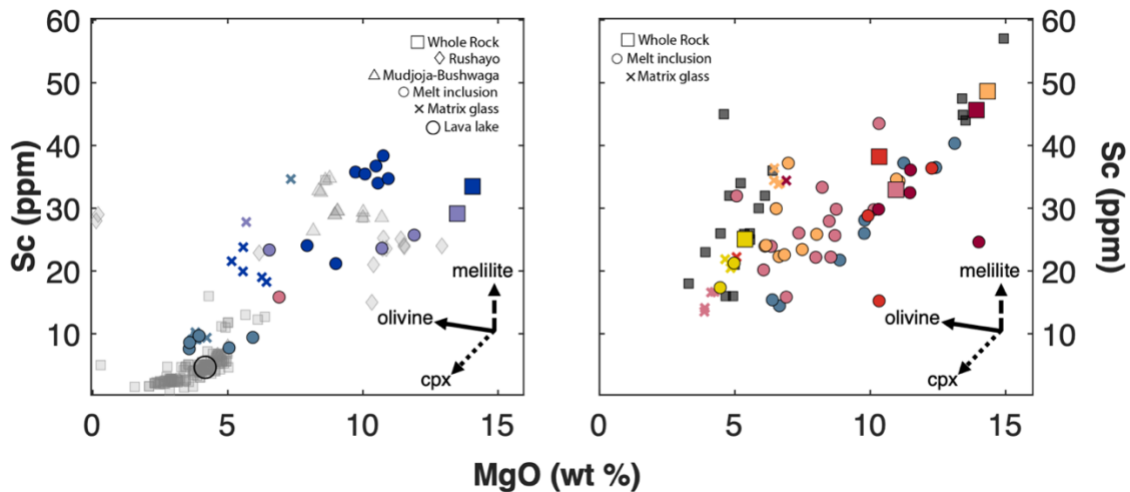


Figure 18. MgO versus Sc at Nyiragongo (left) and Nyamulagira (right). Mineral fractionation vectors are adapted from Molendijk et al. (2023).

clinopyroxene fractionation (**Fig. 18**). Compositions at Nyamulagira show higher initial Sc (~45-50 ppm, with one value at 59 ppm) compared to Nyiragongo (~39 ppm). On a finer scale, whole-rock samples from the Mudjoja-Bushwaga chain and Mugara MI (01T) show higher Sc (25-40 ppm) in comparison to whole-rocks from the Rushayo chain (15-30 ppm Sc). At Nyamulagira, MI, matrix glasses, and whole-rock Sc all show clear correlations with MgO, consistent with clinopyroxene fractionation. Matrix glasses and MI from Mugara are correlated with MgO, consistent with clinopyroxene fractionation as well. Ultimately, whole-rock, MI, and matrix glasses all support clinopyroxene fractionation in our Nyiragongo-type samples rather than melilite. Future studies of MI from the Rushayo chain would be useful for comparing Sc trends to whole-rock data in order to better understand the earliest stages of fractionation from Nyiragongo-type melts.

4.4 Magma crystallization depths beneath the Nyiragongo and Nyamulagira region

Calculated vapor saturation pressures from MI represent minimum pressures and depths for two reasons. First, a volatile-undersaturated melt could have been stored at higher pressures. However, the high and variable CO₂ concentrations in compositionally similar, bubble-restored MI in this study provide evidence that all or nearly all MI were vapor saturated at the time of trapping. Second, although our MI values have been bubble-restored, the presence of carbonate on bubble walls is not accounted for with the Raman + glass method we used, and therefore true pressures of trapping would be higher for any MI where substantial carbonate formation occurred. With regard to this possibility, we note that if the MIMiC-restored CO₂ values are used, our calculated MI entrapment depths increase (up to 23 km depth; **Fig. 19**), making them overlap more significantly with the fluid inclusion depth estimates for Mg-rich olivine from flank cones studied by Louaradi (1994). That study found high CO₂ densities (0.65-0.99 g/cm³) in fluid inclusions in Mg-rich olivine (Fo₈₆₋₈₈), suggesting that magmas crystallize olivine over a wide range of depths in the crust (14-35 km; **Fig. 19**; Louaradi, 1994). This pattern of fluid inclusions extending to higher pressures than melt inclusions has been documented elsewhere (e.g., Métrich et al., 2014). Alternatively, we note that our sample set does not include tephra from either the Rushayo chain or the other cone studied by Louaradi (1993) that yielded the fluid inclusion data, and it is possible that high-MgO magmas beneath these cones

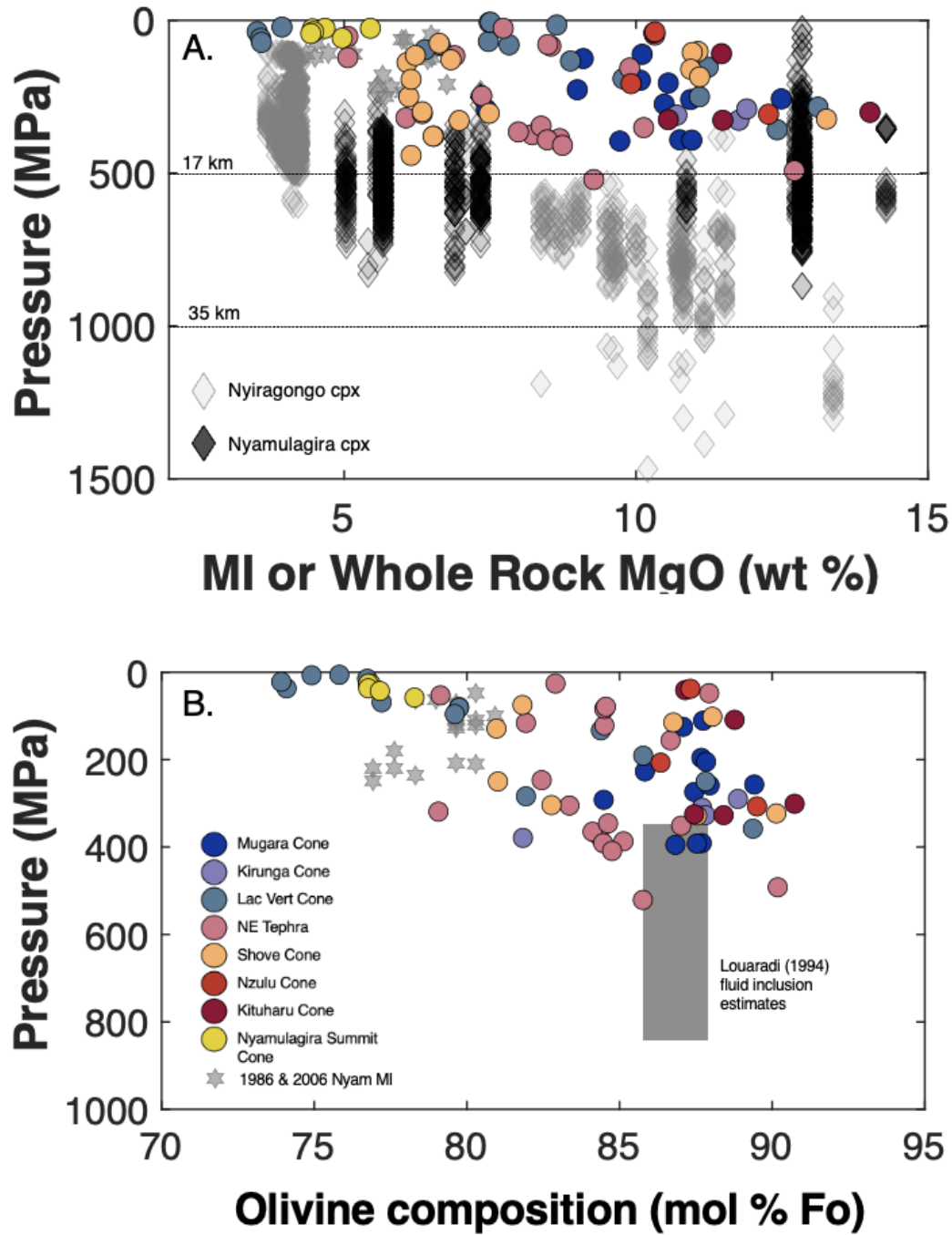


Figure 19. **A.** Comparisons of saturation pressures calculated from olivine-hosted MI versus cpx crystallization pressures calculated from mineral compositions at Nyiragongo (Molendijk et al., 2024) and Nyamulagira (Kamate Kaleghetso et al. 2024). **B.** Comparisons of MI with pressures calculated from fluid inclusions from Louaradi (1994).

crystallized at deeper levels than our samples. Both possibilities could be tested by future combined melt and fluid inclusion studies in this region.

Recent estimates of magma storage at Nyamulagira from Kamate Kaleghetso et al. (2024) applies clinopyroxene-melt and clinopyroxene only thermobarometers using Thermobar (Wieser et al., 2022). The clinopyroxene-melt results on a sample suite that includes higher-Mg flank cone samples indicate a major storage zone at approximately 350–500 MPa (corresponding to depths of 13.2–18.8 km assuming a crustal density of 2.7 g/cm³). This agrees well with the upper range of our MI depth estimates based on either the bubble-restored or MIMiC-restored values, particularly when considering that the cpx-melt barometers they used have a ± 1.4 to ± 2.7 MPa uncertainty. They also considered cpx-only barometers, which have similarly large uncertainties, and a detailed examination of their data suggests the likely presence of both an additional shallower reservoir at ~65–250 MPa (2.5–9.4 km depth) and a deeper one at ~ 600–800 MPa (22.6–30.2 km depth). The shallower reservoir also agrees well with our MI data, and the deeper reservoir or crystallization zones overlap with the deep values for fluid inclusions by Louaradi (1994) for Nyiragongo cones.

Our results from MI show less agreement with the thermobarometric calculations of Molendijk et al. (2024), who applied clinopyroxene-melt thermobarometry (using Masotta et al., 2013) on a sample suite spanning high-MgO compositions from the Rushayo chain to more evolved nephelinites sourced from central vents of Nyiragongo (**Fig. 20**). Their results suggest two primary crystallization levels at 370 ± 90 MPa (evolved lithologies erupted from main the edifice) and 790 ± 170 MPa (primitive lithologies), which translate to $\sim 12.4 \pm 3.0$ and 26.9 ± 5.7 km depths, respectively. The formal uncertainty on the Masotta et al. (2013) barometer is reported as ± 340 MPa, which is relatively large, and this could cause their pressure values for the primitive magmas to be higher than ours. Their values, however, are consistent with the Louaradi (1994) fluid inclusion data. Molendijk et al. (2024) give a thoughtful analysis comparing their pressure results to inferences from seismic data for the region, and interested readers are referred to that discussion.

A potential uncertainty in the use of clinopyroxene-melt barometry in this case is that no such barometers, including Masotta et al. (2013), which is calibrated using trachytes and phonolites, are calibrated for the very low SiO₂ contents of Nyiragongo magmas. As a

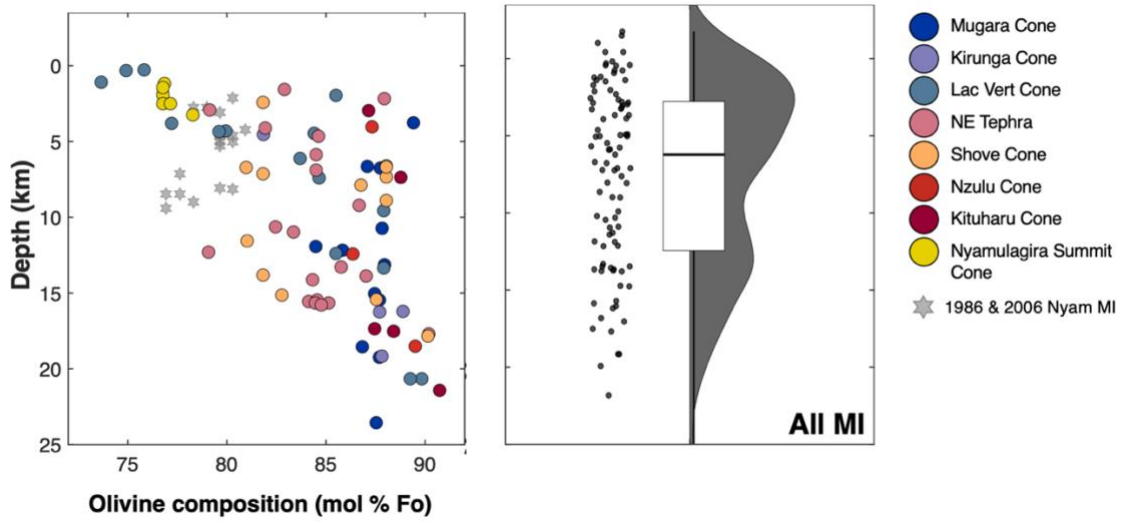


Figure 20. Magma storage depths calculated using MIMiC vapor bubble CO₂ reconstructions.

test of the accuracy of the Masotta et al. (2013) barometer applied to high-Mg Nyiragongo compositions at crustal pressures, we applied the barometer to two experimental clinopyroxenes in a Mount Erebus basanite melt (SiO₂ values of 47 and 44 wt%) equilibrated at 200 and 300 MPa (Iacovino et al., 2016). The barometer predicts pressures of 900 MPa and 2000 Mpa, respectively, for the two clinopyroxenes, suggesting the Masotta calibration may be inaccurate for low SiO₂, strongly silica -undersaturated compositions. On the other hand, tests using experimental clinopyroxenes equilibrated with a high-K arc basalt composition with slightly higher SiO₂ (49 wt%; Di Carlo et al., 2006) shows much better agreement, with deviations on the order of ± 200 MPa. Further work is clearly warranted for better calibration and testing of a clinopyroxene-melt barometer on Nyiragongo compositions, and we note in this regard the recent success of Neave and Putirka (2017) in calibrating a much-improved version of the barometer for tholeiitic compositions at crustal pressures.

For comparison with our results, magma storage depth estimates in the Turkana Depression (Rooney et al., 2022) and Main Ethiopian Rift (Iddon and Edmonds, 2020; Wong et al., 2023) suggest magma storage regions at ~ 12 km depth. In the Main Ethiopian Rift, this depth aligns with seismic signals (Keir et al., 2006; Daly et al., 2008) and fuels the interpretation that focused magmatism facilitates rifting by creating a thermally weak

layer at ~12 km. At the Turkana Depression, Rooney et al. (2022) suggest magma storage is controlled by the lower crustal boundary at ~10 km (Mechie et al., 1994) to explain why magma may pool in this locality. In contrast to the more rapidly extending and higher magma flux Eastern Branch and Main Ethiopian Rift (Saria et al., 2014), in the Virunga Volcanic Province, a mixture of processes influences the depth at which magma pools. Decades of observations show that at Nyiragongo, long, shallowly dipping dikes propagate obliquely to the direction of extension. This process likely facilitates rifting in the region (Muirhead et al., 2015). In contrast, the radial vent alignments at each volcano are likely influenced by overpressure of shallow magmatic systems or edifice loading (Smets et al., 2014). When considering deeply sourced magmas represented by our MI, it is possible that deep magmas ascend towards shallow reservoirs, where they then propagate radially outward from the central edifice. Alternatively, deep magma plumbing systems may be wholly separate. Regardless, when considering the relationship with rifting, deep magma fueling flank eruptions may play a small role in thermally weakening the crust, but shallow dike propagation is the main driver of extension.

4.5 Evidence for carbonatitic metasomatism from Zr/Hf ratios?

Carbonate-bearing metasomes formed from carbonatitic melts are frequently invoked as a source component for CO₂-rich magmas in the Virunga and Toro Ankole Provinces based on major, trace element and isotopic datasets (Furman and Graham 1999; Rosenthal et al., 2009; Chakrabarti et al., 2009a; Pitcavage et al., 2021; 2024; Innocenzi et al., 2024). At Nyiragongo, high Zr/Hf ratios (45-100) compared to typical values of 33-40 for MORB, flood basalts, and orogenic basalts (Jochum et al., 1986) have been considered indicative of carbonatitic metasomatism in the mantle because carbonatite melts have high Zr/Hf and impart high ratios to metasomatized mantle (Dupuy et al., 1992). Primitive whole-rock samples from Nyamulagira have Zr/Hf ratios of 33-43, identical with the range of values (34-44) for the Mudjoja-Bushwaga chain, but lower than values of 40-60 for the Rushayo chain (**Fig. 21**). Primitive Nyiragongo-type and Nyamulagira-type MI have Zr/Hf of 39-48, and the highest Zr/Hf values are found in the Mugara MI (01T; average = 44). The range of values for MI overlaps for the most part with MORB ranges (~37.5 +/- 6.8;

Arevalo and McDonough, 2010), and thus does not provide much support for source enrichment by carbonatitic metasomatism. However, the Rushayo Zr/Hf ratios are distinctly higher than MORB, and the highest values overlap with the lower part of the range of Zr/Hf for western EARS carbonatites (**Fig. 23a**). Because Rushayo chain primitive rocks are the most likely candidates for parental magmas to Nyiragongo, the high Zr/Hf at Rushayo suggests a possible role for carbonatitic metasomatism in the Nyiragongo source.

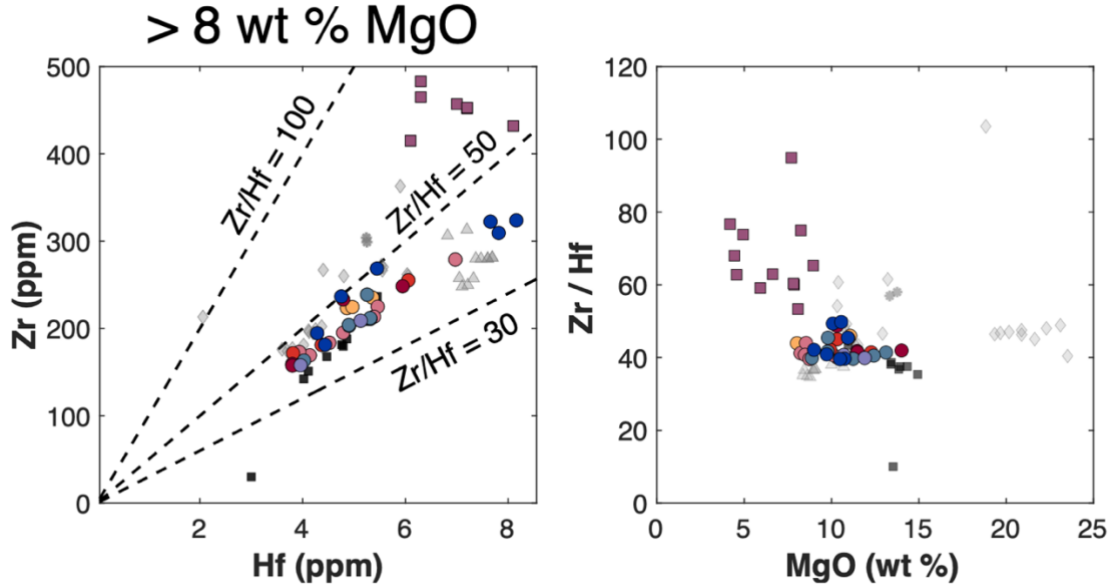


Figure 21. Zr/Hf ratios of primitive whole-rock and MI. MI = colored circles, primitive Nyamulagira = black squares, Rushayo chain = gray diamonds, Mudjoja-Bushwaga chain = gray triangles, Mugogo flow = gray asterisks, Western branch carbonatites = purple squares.

Zr/Hf ratios of primitive lavas from Bufumbira are 22-45 (Pitcavage et al., 2023), and while these values were used to suggest carbonated metasomatic lithospheric sources, the wide range of Zr/Hf and large extent of overlap with MORB values is inconclusive. Exceptionally high (70-100) Zr/Hf ratios are only present in highly evolved Nyiragongo samples, suggesting crystal fractionation plays a role in modifying this trace element signature at lower MgO. Experimental work from Minissale et al. (2019) and Molendijk et al. (2023) both showed that Hf is moderately more compatible than Zr in evolved clinopyroxene (D_{Hf} : 1.58 and 3.88; D_{Zr} : 1.02 and 2.26). Given the low abundances of Hf,

subtle differences in compatibility could reasonably change Zr/Hf ratios. Crystallization of perovskite, present as an accessory mineral in more some evolved samples (Platz et al., 2004; Molendijk et al., 2024), could also affect Zr/Hf ratios.

4.6 Evidence for involvement of subduction zone fluids from Li/Yb?

Hudgins et al. (2015) interpreted high Li/Yb ratios (11-12) in Bufumbira MI as a signature of mobile, subduction-sourced fluids. In comparison to Bufumbira samples, MI from our dataset exhibit significantly lower Li concentrations (2-12 versus 2-57 ppm Li). As a result, Li/Yb ratios in our MI data only extend to 3.5, and the ratio clearly increases during differentiation (**Fig. 22**), suggesting the possibility of Li increasing due to contamination by crustal materials (e.g., Walowski et al., 2019). Li diffuses very rapidly through olivine, so the high Li values in the Bufumbira MI could also potentially have been generated by diffusion of Li into the MI during experimental rehomogenization.

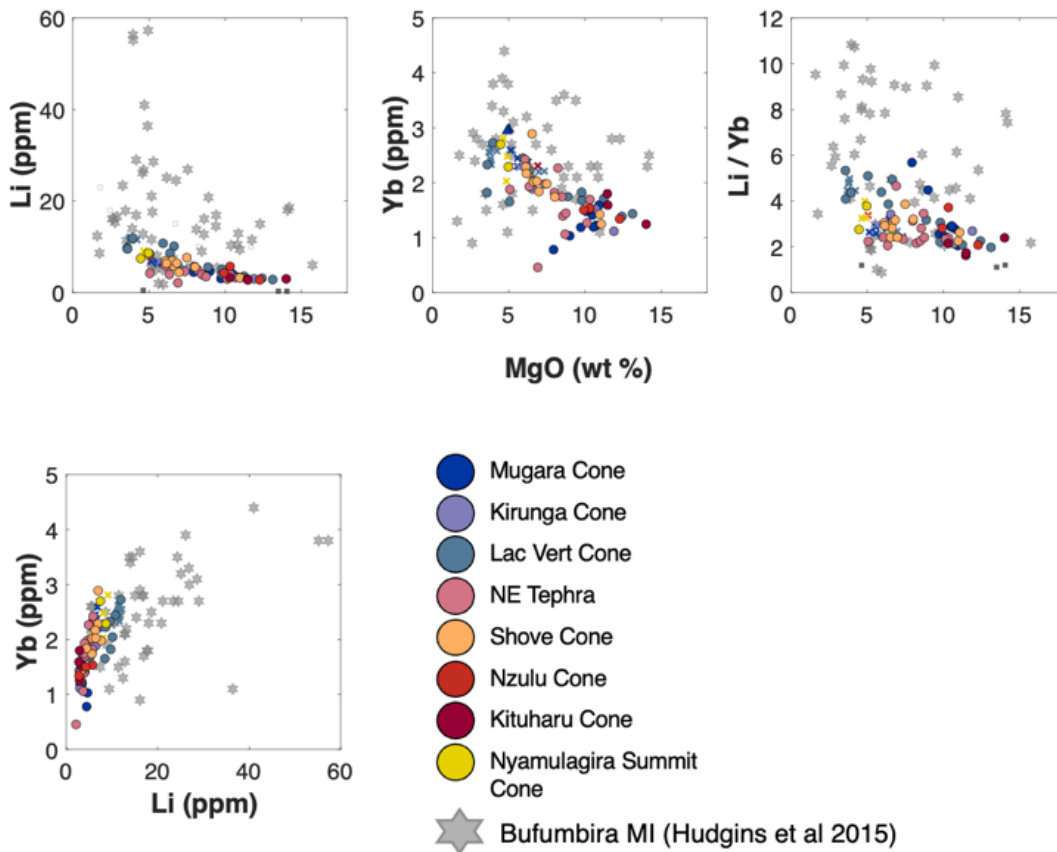


Figure 22. Trace element data from MI (this study) and rehomogenized Bufumbira MI (Hudgins et al., 2015).

4.7 Characterizing magma source mineralogy and composition

Given the lack of direct constraints from xenoliths, we compare primitive MI and whole-rock compositions to experimental glasses generated by partial melting of various starting materials (**Fig. 23**). Starting materials for the experiments of Foley et al. (1999) contain varying modal proportions of amphibole, clinopyroxene, biotite, and apatite, whereas experiments from Medard et al. (2006) and Pilet et al. (2008) contain mixtures of olivine, clinopyroxene and amphibole. Partial melting experiments from Lloyd et al. (1985) on nodules from southwestern Uganda include clinopyroxene and phlogopite, with minor titanomagnetite, sphene, and apatite. Experiments from Foley et al. (2022) include K-richterite, phlogopite, and clinopyroxene. Lastly, the experiments of Grützner et al. (2023) were reaction experiments between amphibole-clinopyroxene metasomes and lherzolite. Considering the low SiO₂ and high CaO contents in the primitive MI, we filtered experimental melts from starting assemblages containing amphibole to CaO and SiO₂ contents greater than 10 wt% and less than 46 wt%, respectively. Melts of K-richterite-bearing assemblages (Foley et al., 2022) typical of MARID xenoliths from continental cratons and clinopyroxene-phlogopite nodules (Lloyd et al., 1985) contain too much K₂O (3.8-8.5 wt%) to produce primitive Nyiragongo and Nyamulagira melts (Fig. S25). In contrast, garnet lherzolite melts have Na₂O/K₂O that is too high. As discussed in the text, the experimental melts from Foley et al. (1999) that included amphibole±biotite provided the closest match to the Na₂O and K₂O contents of primitive Nyiragongo and Nyamulagira melts.

The metasome model is frequently invoked to explain the origin of melts with very low SiO₂ because such melt compositions require a low-Ca-pyroxene-free (non-peridotitic) source region (Prelević et al., 2024). However, the results of Sun and Dasgupta (2020), which we used in our metasome plus wall-rock melting model for estimating final melt CO₂ concentrations, show that carbonated lherzolite melting can generate melts with low SiO₂ values. For carbonated lherzolite to serve as a potential source rock for Nyiragongo

and Nyamulagira primitive magmas, it would likely need to be a metasomatized peridotite with modal amphibole and phlogopite to achieve the right Na_2O and K_2O concentrations.

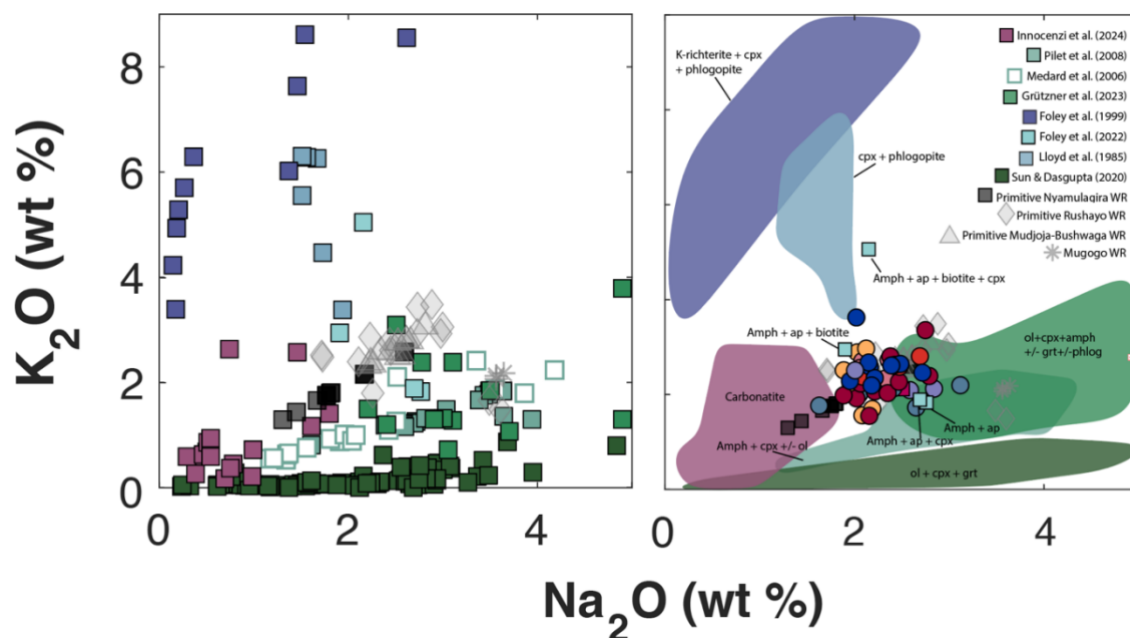


Figure 23. Experimental data used to generate compositional fields in Figure 9 in the main text. Experimental partial melts of various amphibole- and/or phlogopite-bearing mafic and ultramafic assemblages shown by symbols (A) and colored fields (B). References are shown in B. Note that the starting materials of Foley et al. (1999) used biotite rather than phlogopite. Also shown are carbonatites from the western Branch of the EARS (Innocenzi et al. 2024), primitive (>8 wt % MgO) whole-rock samples from Nyamulagira and Nyiragongo, and our MI data (in panel B).

For example, partial melts of garnet lherzolite with H_2O and CO_2 at 3 GPa have low SiO_2 (41-47 wt%) but $\text{Na}_2\text{O} > \text{K}_2\text{O}$, as expected from their relative abundances in the starting material (Baasner et al., 2016). The experiments of Stamm and Schmidt (2017) involved forced saturation of a kimberlitic melt with lherzolite mineralogy at high pressure (7 GPa) in a CO_2 -rich system. In this case the experimental partial melts contained very high alkalis (~ 10 -15 wt.%) and very low SiO_2 (~ 4 -25 wt.%), which are unlike high-Mg magmas in the Virunga region.

To estimate Cl and F concentrations of amphibole and biotite, we use recently published data from a global compilation of Hecker et al. (2020). Their measurements show that in contrast to F-rich hydrous phases in kimberlites, amphibole and phlogopite from mantle samples exhibit a wider range of F (0.12-0.87 wt%) and Cl (100-600 ppm), which

they propose is caused by progressive desiccation of fluids during reaction and crystallization in the mantle. Using recently published D_F and D_{Cl} from Flemetakis et al. (2021) and median halogen concentrations in amphibole and phlogopite (1020 ppm F and 630 ppm Cl in amphibole; 3890 ppm F and 350 ppm Cl in phlogopite; Hecker et al., 2020), and assuming negligible halogens in clinopyroxene, the resulting melting models (**Fig. 9c-d**) show that after amphibole and phlogopite are consumed in the source, F/Cl ratios of high degree melts reach a plateau. The same pattern is seen with the F/Nd ratio during melting (**Fig. 24**). The median F values from Hecker et al. (2020) produce melt F

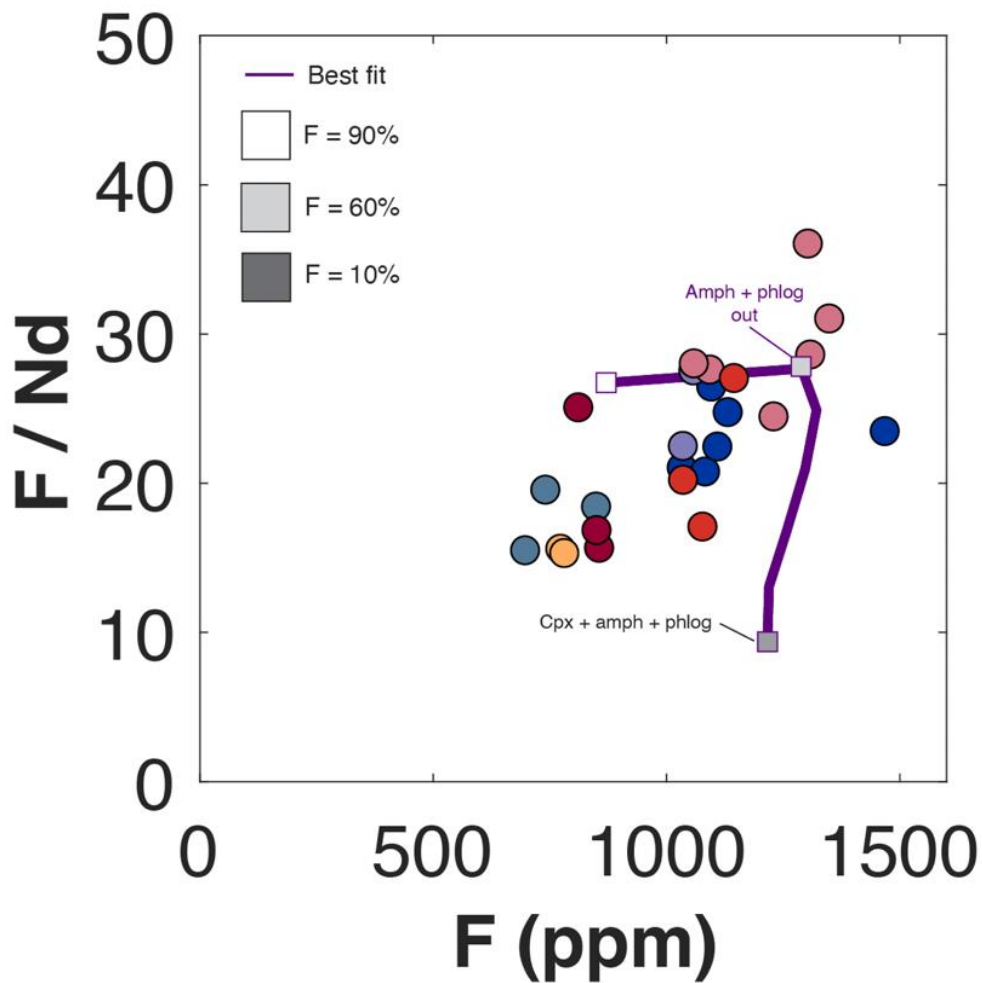


Figure 24. Partial melting model of an amphibole+biotite+clinopyroxene assemblage with an initial bulk concentration of 25 ppm total Nd.

2.6, average MI $F/Cl = 1.8$). These models align closer to the MI F and Cl data than models that use the Flemetakis et al. (2021) amphibole and phlogopite compositions, which when concentrations that are similar to our MI but overpredict melt F/Cl ratios (modeled $F/Cl =$ used in the melting model yield F contents and F/Cl ratios that are far higher (>5300 ppm F , $F/Cl=20$) than any MI values found in the EARS or at OIB settings. To best fit our data, we use median F contents from Hecker et al. (2020) but increase initial Cl concentrations to 820 and 585 ppm in amphibole and phlogopite, respectively, resulting in F/Cl ratios stabilizing at ~ 1.8 when amphibole and phlogopite are melted. While higher than median mantle xenolith Cl concentrations, these Cl values are still within the measured range of both phases, and thus are still reasonable.

Because Nd has similar incompatibility as F during mantle melting, we also modeled its behavior. To best fit our dataset, we assume a source concentration of 20 ppm of Nd . This value is higher than concentrations of 0.7-4.9 ppm Nd from Flemetakis et al. (2021), but much lower than 200-300 ppm Nd estimated in metasomes by Rosenthal et al. (2009). In our non-modal melting model, we calculate bulk D_{Nd} (ranging from 0.05-0.11) at each melting step, where Nd is incompatible in all phases, but the least incompatible in clinopyroxene and amphibole.

5. Bridge

Chapters II and III have a broad goal in using microscopic features in minerals to answer fundamental questions related to magma sources, storage, and degassing processes. These processes, from melt generation to CO_2 emission, occur over large temporal and spatial scales. In Chapter IV, we narrow our focus to analyze the years, months, days, and hours preceding eruptions. Predicting the timescales between unrest signals at volcanoes and eruptions is vital for hazard management. Given the lack of flank eruptions in the modern record, it is unclear how precursory unrest or activity at flank cones may compare with summit or near summit eruptions. Using mineral zoning patterns, we analyze magma transport pathways prior to flank eruptions and model the timescales between eruptions and their potential triggers (i.e. magma mixing). To calculate these timescales, we employ a technique called diffusion chronometry, in which the diffusion of cations within minerals

is modeled. To approximate the rate of elemental diffusion it is vital to have robust constraints on magma storage conditions at both volcanoes. Using data from melt inclusions in Chapters II and III, we can input estimates of temperature, pressure and f_{O_2} into our models, which enabled us to more accurately estimate rates of diffusion at magmatic conditions. It would not be possible to conduct the study presented in Chapter IV without the groundwork investigations done in Chapters II and III.

CHAPTER IV:TIMESCALES OF MAGMA MIXING AND ASCENT AT NYIRAGONGO AND NYAMULAGIRA DEMOCRATIC REPUBLIC OF THE CONGO

This work is in preparation to submit to the *Bulletin of Volcanology* with Lissie Connors as lead author, with co-authors Paul J. Wallace (University of Oregon) and Kenneth W.W. Sims (University of Wyoming). This project was developed by Lissie Connors, Paul J. Wallace, and Kenneth W.W. Sims. Sample collection was led by Kenneth W.W. Sims. Data collection and numerical modeling was led by Lissie Connors. Writing was led by Lissie Connors and Paul J. Wallace.

1. Introduction

Precursory volcanic signals operate on a range of tempos. Some eruptions seem to occur without any warning, whereas others produce signals for years prior to eruption (Girona et al., 2021). Understanding the processes that lead to eruption and the timescales associated with them is vital for constraining the hazards at any particular volcano. Recent technological advances are increasing our ability to monitor volcanoes more continuously, at higher resolutions, and with lower risk to the scientists studying them. With these growing capabilities, precursory signals of unrest for modern eruptions are giving clearer, more holistic pictures of processes happening within magmatic plumbing systems. Petrologic studies of active volcanoes can be complementary to monitoring efforts, constraining the depths of magma storage (e.g. Cashman and McConnell, 2005; Dayton et al., 2021; Lerner et al., 2021), identifying characteristics of melt batches, or elucidating eruption triggering mechanisms. For frequently active volcanoes, such as Kilauea (Lynn et al. 2024; Mourey et al. 2023), Etna (Kahl et al., 2011), or Llaima (Ruth et al., 2018), petrologic studies have shown how eruptions repeatedly utilize similar magma transport zones or pathways, showing how past eruptions can be used to better understand likely characteristics of future eruptions.

In magmatic systems, the processes governing the composition of crystallizing minerals are constantly competing between thermodynamics and kinetics. While

thermodynamically based petrologic tools assume a crystal in equilibrium with its environment, the presence of compositional zoning resulting from variable thermal and/or compositional regimes shows the importance of kinetic processes. By coupling experimental constraints on elemental diffusivities (Dohmen and Chakraborty, 2007) and numerical models solving Fick's 2nd law (Girona and Costa, 2013), the diffusion-based relaxation of compositional gradients in minerals can be modeled to obtain timescales. In the past decade this technique, referred to as diffusion chronometry, has been applied to modern and historic eruptions using a range of elements and mineral phases. Focusing on the common phenocryst mineral olivine, zoned crystals from mafic eruptions have yielded timescales of days to months between magma mixing events and eruption, frequently aligning with monitoring signals of unrest. For historic eruptions with no modern monitoring data, diffusion chronometry can be a particularly helpful method to estimate the potential timescale between unrest and eruption. Despite its utility, diffusion chronometry techniques have not been applied at volcanic systems in the East African Rift System, which erupt frequently, pose significant risk to large populations, and are relatively understudied among volcanic systems (Biggs et al., 2021).

2. Geologic setting

The East African Rift System (EARS) is home to >70 active volcanoes, with 21 erupting in the past 200 years (Wadge et al., 2016). Eruptive products in the EARS are spatially and temporally diverse, from effusions of flood basalts in the Main Ethiopian Rift, to Plinian eruptions of peralkaline rhyolites in the Rungwe Volcanic Province, to natrocarbonatite flows at Oldoinyo Lengai. The hazards posed at rift systems are equally variable, from high magnitude tectonic earthquakes ($M_w \sim 6.8$ at Lake Tanganyika; Mavonga 2007), exceptionally low viscosity lava flows (Nyiragongo: Komorowski et al., 2002), and catastrophic lake overturns (Lake Nyos 1986: Kling et al., 1986). Of the volcanic systems in the EARS, Nyiragongo and Nyamulagira Volcanoes, in the Democratic Republic of Congo (DRC), erupt with the most frequency. Just 15 km apart from one another, these volcanoes erupt every ~1-4 (Nyamulagira; Smets et al., 2015) and

approximately every 30 years (Nyiragongo; Pouclet and Brahm 2021), respectively, and Nyiragongo has a long-lived lava lake in its summit caldera.

Studies at Nyiragongo dating back to 1894 (Sahama and Meyer, 1958) highlight its lava lake as unique globally. In the past century, observations of the lava lake show dramatic oscillations in lake level (e.g; Pouclet 1976; Tazieff 1985), periodic crater eruptions (Barrière et al., 2022), and continuous degassing of CO₂-rich plumes (Sawyer et al. 2008; Boudoire et al., 2022). Recent eruptions in 1977, 2002, and 2021 all involve draining of the lake to fuel catastrophic lava flows erupted from near-flank vents. Eruptions at Nyiragongo have been devastating, with the 2002 eruption killing ~147 people, displacing thousands, and damaging ~15% of the city (Tedesco et al., 2007). Since then, a growing number of people fleeing regional violence have come to Goma to seek safety in its administrative boundaries (Michelier et al., 2020), posing numerous challenges to addressing population needs during a crisis (Syavulisembo et al., 2024). Nyamulagira, ~15 km northwest of Nyiragongo, poses different hazards. Located in a more remote region of Virunga National Park, lava flows from Nyamulagira have historically flowed over 20 km into populated regions in Sake and around Lake Kivu (Smets et al., 2010). While posing relatively less risk to civilians, the remote location of Nyamulagira makes monitoring efforts challenging, as these regions have been episodically occupied by militant groups.

Researchers seeking to better constrain hazards have mapped the likely paths of future lava flows (Kervyn et al., 2024), and this has been complemented by work on enhancing community preparedness (Mafuko-Nyandwi et al., 2024). One hazard still poorly constrained in the region is the threat posed by eruptions on the distal flanks of both volcanoes (>10 km from the caldera center). These eruptions, typically smaller in volume compared to recent lava flows, have occurred as recently as 1991 at Nyamulagira (Mikombe: Kasahara et al., 1991; Smets et al., 2015), and likely within the past 500 years at Nyiragongo (Kirunga: Poppe et al., 2016; Wood and Sholz, 2010). Along the southern flanks of both volcanoes, eruptions near and within Lake Kivu have created dozens of mono- and polygenetic cinder cones, maars, tuff rings, and sublacustrine edifices. Hazards associated with phreatomagmatic eruptions can be especially dangerous, generating dilute

pyroclastic density currents that can travel 1-5 km from the vent site (Brand et al., 2014). Purely magmatic eruptions forming cinder cones along the distal flanks pose their own hazards, including ash fall and ballistics. While distal eruptions on the northern flanks occur in relatively remote regions, distal eruptions in the southern flanks affect more dense population centers. For this reason, understanding the processes that lead to these eruptions, and the timescales associated with them is vital to understanding the hazard potential these volcanoes pose.

3. Materials and Methods

3.1 Samples

Tephra samples from cinder cones, tuff rings, and maars in this study were collected on a field expedition in 2015 (**Fig. 1**; Phillips 2015), and are predominantly sourced from the southern flanks of both edifices. At both volcanoes, most vents are aligned along radial fissure systems from each edifice. Nyiragongo exhibits three major alignments in the NE-SW (Rushayo; DRC17T [Lac Vert tephra]), N-S (Mudjoja-Bushwaga; DRC01T [Mugara cone]), and E-W (Nyamushwa; DRC31 [NE flank tephra outcrop]) directions (Demant et al., 1994). Tephra sample DRC39 [Kirunga tephra outcrop] is slightly offset from the Rushayo chain. At Nyamulagira, two fissures, oriented NW-SE, and continuing SE-NW on the other side of the caldera show concentrated vents, with several vents spaced independent of fissure systems (Smets et al., 2015).

Nyamulagira tephra in this study were not erupted from sources located within vent alignments. Sample DRC23T is from Shove cone, a massive cinder cone 18 km away from Nyamulagira's summit, and is assumed to be pre-Holocene in age based on its degree of weathering (Pouclet 1976). Even further from Nyamulagira, Nzulu (DRC21T; also referred to as N'zuru) and Kituharu (DRC22T) are tuff rings (Denayer, 1975).

Major and trace element compositions of bulk tephra samples (**Fig. 2**) and volatile, major, and trace element geochemistry of olivine-hosted melt inclusions were previously characterized by Connors et al. (*in review*).

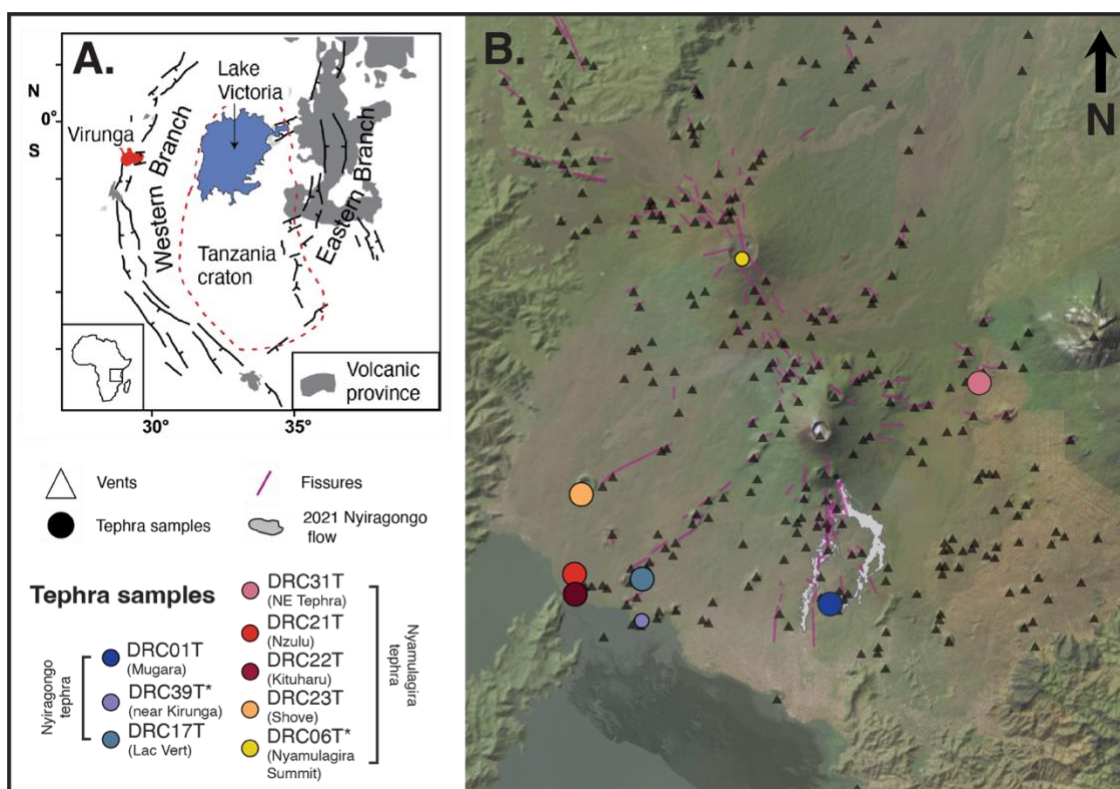


Figure 1. A. Map of the East African Rift, with Virunga Volcanic Province indicated in red. B. Locations of tephra samples. Flank vent and fissure locations are from Smets et al. (2014); lake bathymetry is from Ross et al. (2014). Black triangles indicate subaerial vents, white triangles indicate vents along the current floor of Lake Kivu. Samples DRC39T and DRC06T (smaller symbols on map) have major and minor element data for olivine, but no traverse data was collected.

3.2 Analytical methods

Olivine phenocrysts with adhering glass were picked from hand-crushed tephra samples. Using methodologies from Lynn and DeSmithers (2023) as a guide, olivine crystals were aligned and set in crystal bond perpendicular to their b-axes (**Fig. S1**). As significant uncertainty arises from anisotropic diffusion (Shea et al., 2015) and sectioning effects (Wallace and Bergantz, 2004), orienting minerals before analysis can minimize uncertainties. Crystals from Lac Vert are much smaller and fragmented compared other tephra samples, and were not oriented to the same accuracy. After the crystal bond cooled, olivine crystals were carefully ground and polished individually (down to 1 μm abrasive) to expose their cores. The sectioned olivine were then mounted in epoxy. Epoxy mounted samples were then repolished to a 0.5 μm finish. A subset of olivine phenocrysts were

mounted in indium using a vice and hydraulic press. Samples were then carbon-coated for microbeam analyses. Back-scatter electron (BSE) images were collected for all olivine phenocrysts using a FEI Quanta 200 SEM in 2021 and ThermoFisher Scientific Apreo 2 SEM in 2024. Using ImageJ software (Schneider et al., 2012), we identified zoning patterns present in crystals and used the results to plan optimal transect locations for electron microprobe analysis (EPMA). Target transects were identified by plotting profiles of grayscale values averaged across a 50 μm rectangular field of view, identifying areas parallel to the a or c- axis with the steepest grayscale gradients. To ensure analyses reached as close to the crystal-melt interface as possible, we preferentially selected regions next to adhering matrix glass. Transect data was collected at the University of Oregon using a Cameca SX100 electron microprobe using Probe for EPMA. Core and rim analyses of 190 olivine phenocrysts were collected, as well as 41 transects.

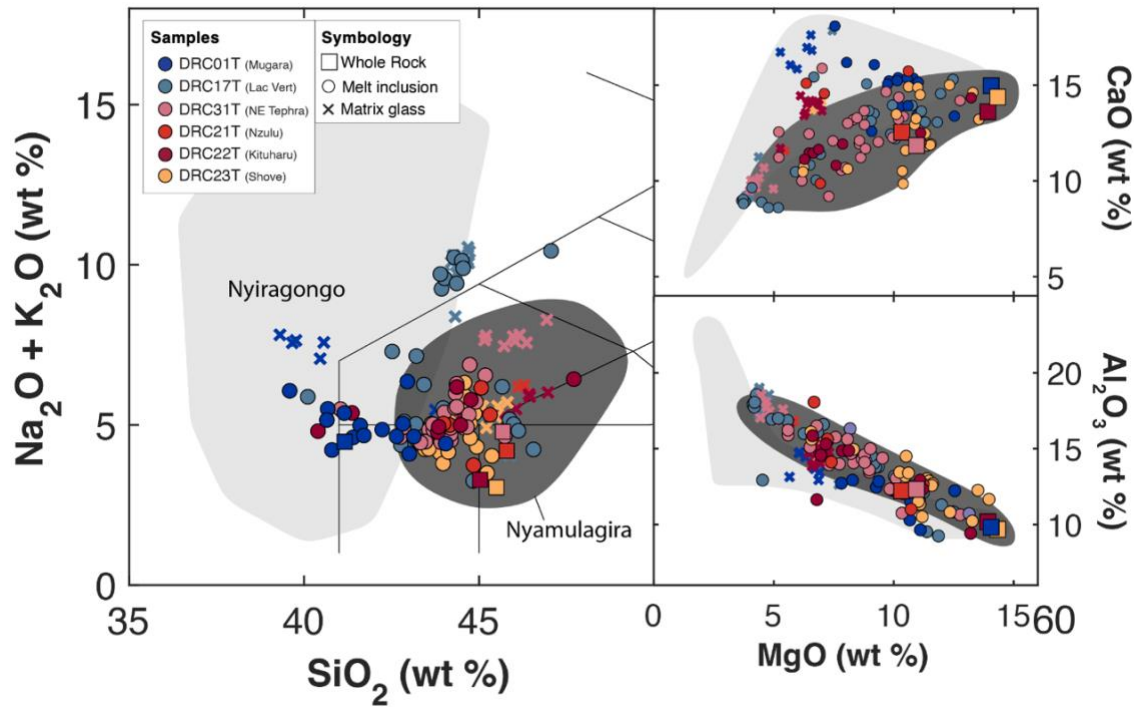


Figure 2. A. Total alkalis versus silica diagram showing compositions of tephra samples, melt inclusions, and matrix glasses (Chapter II) Gray field indicates whole rock samples from Nyiragongo, black field indicates whole rock samples from Nyamulagira. Squares denote bulk tephra XRF analyses, circles denote melt inclusion analyses, and x's denote matrix glass analyses. CaO versus MgO (B) and Al_2O_3 versus MgO (C), with the same symbols as A.

Major, minor, and trace elements in olivine were analyzed in 2020, 2021, and 2024. Olivine phenocrysts were collected every 2-20 μm using a 1 μm focused beam, an accelerating voltage of 20 kV, and current of 30 nA for Si, Fe, Mg, and current of 200 nA for Ca, Cr, Ni, Mn, and Al. To test the effect of diffusion anisotropy, a subset of transects were taken in both the a and c directions. Peak counting times for Si, Fe and Mg were 40 seconds, with off peak counting times of 5 s on each side. Count times for minor and trace elements were longer (Ca, Cr, Mn: 40 on peak, 40 off peak; Ni, Al: 45 on peak, 45 off peak). A mixture of natural and synthetic standards were used for calibration, using synthetic forsterite for Si and Mg, magnetite for Fe, Chesterman diopside for Ca, nepheline for Al, synthetic MnO for Mn, synthetic NiO for Ni, and chromite for Cr. Detection limits were 0.003 wt% for Al_2O_3 , 0.003 wt% NiO, 0.012 wt% MnO, and 0.003 wt% CaO. Analytical precision (expressed in relative standard deviation) is less than 1% for SiO_2 , MgO, CaO, MnO, NiO, Al_2O_3 less than 1.3% for FeO and Cr_2O_3 , and less than 2% for P_2O_5 . Analyses with totals below 98.5 and above 101.5 were excluded from the dataset.

To add spatial resolution to our transect data, and enable the modeling of olivine with BSE images alone, we used measured transects to convert BSE grayscale values to forsterite concentrations (Martin et al., 2008). Using a python code from Aufrere et al. (2024), we extracted a linear relationship between olivine Fo content and grayscale values by matching EPMA-analyzed values and grayscale values at the same distances along the profile. To ensure quality, we did not model grayscale profiles where R^2 values were below 0.9. For olivine with BSE imagery and no EPMA measurements, we used the equation from the highest R^2 value grain within the same tephra sample. The epoxy mount olivine Fo versus grayscale calibration was only applied to olivine in epoxy mounts, and similarly, we used the indium mount olivine Fo versus grayscale calibration for olivine in indium mounts, as the contrast is not comparable between samples in different mounting mediums. Eighty-three transects were generated in this manner, and yielded transects with 0.5-2 μm point spacing (compared to 5-20 μm spacing from EPMA data).

Concentrations of hydrogen (H^+) in olivine were measured using a Thermo-Nicolet iN10 infrared microscope at Montana State University. Doubly polished olivine wafers were oriented perpendicular to the b-axis using the same methodology used for microbeam samples and were polished to a thickness less than 200 μm . Olivine thicknesses were then

measured with a digital micrometer. We collected a mix of spectra that were unpolarized, polarized parallel to the c-axis, and polarized parallel to the a-axis (Fig S8). Spectra were collected with an aperture of 100x20 μm , a resolution of 4 cm^{-1} , and 256 scans. Collected absorption spectra were fit with a polynomial baseline through wavenumbers 3150 and 3650 cm^{-1} , and integrated absorbances were multiplied by an absorption coefficient (0.119) from Withers et al. (2012) to convert to H_2O concentrations. Since absorption normal to the IR-parallel plane (in this case, the b-axis) was not measured, we multiply absorbances by 2.1, according to methodologies in Barth et al. (2023).

3.3 Modelling methods

To model the timescales producing Mg-Fe and Ni profiles in our olivine data, we modify a forward model (Mourey et al., 2023) that employs an explicit finite difference method to solve Fick's 2nd law (Eq. 1) in its discretized form in one dimension (Eq. 2).

$$\frac{\partial C_i x}{\partial t} = \frac{\partial}{\partial x} \times D_i \times \frac{\partial C_i(x,t)}{\partial x}. \quad (1)$$

$$C_{i,t+1} = C_{i,t} + D\Delta t \left[\frac{C_{i+1,t} - 2C_{i,t} + C_{i-1,t}}{\Delta x^2} \right] \quad (2)$$

To approximate the rate of Fe-Mg interdiffusion, we use an expression of diffusion perpendicular to the c-axis (Eq. 3) from Dohmen and Chakraborty (2007). As diffusion in olivine is anisotropic (Dohmen and Chakraborty 2007; Chakraborty 2010), Fe-Mg diffusion parallel to the a and b axes is approximately six times slower than diffusion parallel to the c-axis. Similarly, we use the expression of Chakraborty (2010) to calculate diffusivity of Ni in olivine (Eq. 4). All diffusivities are expressed in m^2/s , and use f_{O_2} in Pa, X_{Mg} and X_{Fe} in mole percent, pressure in MPa, and temperature in Kelvin.

$$D_c^{\text{Fe-Mg}} = 10^{-9.21} \times \left(\frac{f_{\text{O}_2}}{10^{-7}}\right)^{1/6} \times 10^{3(X_{\text{Mg}}-0.9)} \exp\left(-\frac{Q + (P - 10^5) \times 7 \times 10^{-6}}{RT}\right) \quad (3)$$

$$D_c^{\text{Ni}} = 3.84 \times 10^{-9} \times \left(\frac{f_{\text{O}_2}}{10^{-6}}\right)^{1/4.25} \times 10^{1.5(X_{\text{Fe}}-0.1)} \exp\left(-\frac{Q + (P - 10^5) \times 7 \times 10^{-6}}{RT}\right) \quad (4)$$

Using this method, best fitting timescales are chosen using the root-mean-square method (Girona and Costa 2013) (Eq. 5), in which N is the number of points in the profile, C is the concentration (Forsterite, in mol%), j specifies the position along the profile. Because many of our profiles have flat, homogeneous cores, we modified the model to specify ‘fitting zones of interest’ for each profile. With this modification, users can input a range of x -values along the profile where the fit is most important for constraining the diffusion timescale, and the model will multiply the residual by 10 within this range. If no region is specified, then all regions are accounted for equally.

$$RMSD = \sqrt{\frac{\sum_N \left((C_{modeled}^j - C_{measured}^j) \times Fo_{weight}^j \right)}{N}} \quad (5)$$

To assign errors to best fitting timescales, we primarily focus on the effect of uncertainties in magma temperature on estimated timescales, using a modification of an uncertainty calculation (Eq. 6) from Girona and Costa (2013), where τ is similar to the diffusion coefficient with temperature term removed. The magnitude of errors (expressed in days) correlate with the timescales, and inversely correlate with temperature.

$$\begin{aligned} \sigma_t^+ &= \Delta t + t_{best\ fit} + e^{\tau \left(\frac{1}{T} - \frac{1}{T - \sigma_T} \right)} T - 1 \\ \sigma_t^- &= \Delta t + t_{best\ fit} + 1 - e^{\tau \left(\frac{1}{T} - \frac{1}{T - \sigma_T} \right)} T - 1 \end{aligned} \quad (6)$$

For most forward models of diffusion, the user must input assumed initial olivine Fo and Ni profiles for the composition prior to diffusive modification, and then iteratively modify the composition until an reasonable fit is achieved. For most olivine in our dataset, which exhibit a thin rim and homogeneous core, a simple step function is an appropriate initial profile (Fig 8). For olivine with more complexly-zoned interiors, only profiles of the outer rim are fit. In both cases, one must make an assumption of precisely where along the x axis the change in concentration falls. While minor and trace element concentrations may indicate where a growth zone began (e.g. Lynn et al., 2024), an empirically defined step location may be just as functional. We have modified code from Mourey et al. (2023) to allow for the input a range of x -values along the traverse where the concentration change may occur. Then, we have added an additional loop that randomly varies the location of

the step function within the defined x value range for a specified number of iterations. With this new functionality, the best fitting time timescale and initial step location is determined for each olivine.

To model diffusion timescales of H^+ in olivine during magma ascent, we apply a methodology from Newcombe et al. (2020). Ascent chronometry in this case assumes that decompression-driven degassing drives dehydration of the olivine phenocryst, as solubility of H_2O decreases in the melt. In this 1D method, a Monte Carlo approach is used for varying the measured H_2O contents by analytical uncertainties, varying estimated K_d for H^+ in olivine, and varying the diffusivity of H^+ . However, it does not vary the boundary conditions in the same way. While this method still numerically solves the diffusion equation, it is critically different from the major element diffusion models employed here in its assumption of decreasing H_2O content along the olivine-melt interface with time. In this case, an ascending magma is approximated by inputting a degassing path, which we modeled in MafiCH (Allison et al. 2021), using an initial water content of 1.2 for measured 21T [Nzulu] olivine. For each step in pressure used in the model, the corresponding H_2O concentration is applied as a boundary condition.

4. Results

4.1 Olivine compositions

Olivine phenocrysts analyzed in this study are variable in size (Fig. S2; 0.5-1.1 mm parallel to the a or b axis, 0.5 to 2.6 mm parallel to the c axis). Olivine from the Lac Vert tephra are the smallest and most equant, whereas olivine from other cones are larger and more elongate. Across samples, crystal habits of olivine are generally euhedral, with sharp boundaries at the crystal-melt interface. Some euhedral crystals show dendritic growth textures along the crystal corners. Olivine from DRC31 [NE flank tephra] exhibit cellular textures along their rims, with narrow lobes distributed along the entirety of the crystal rim (Fig S6). Phenocrysts from all samples typically contain small inclusions of Cr-spinel.

Most olivine in the different samples are normally zoned (85%), with a small subset of reversely zoned crystals. From this point onward for simplicity we will refer to $>Fo_{85}$ olivine as primitive and $<Fo_{85}$ as evolved. Zoned rims range from 15 to 50 μm in length for primitive olivine, and 75 to 105 μm for evolved olivine. The highest Fo concentrations in olivine cores (up to Fo_{91}) come from the Nzulu (DRC21T), Kituharu (DRC22T), and Shove (DRC23T) tephra, followed by Fo contents (up $Fo_{89.5}$ and $Fo_{88.5}$) from the Mugara and NE tephra, respectively. Nzulu and Kituharu both show a mixture of normally and reversely zoned olivine (Fig. 4), with normally zoned cores showing compositions between Fo_{91-85} and reversely zoned cores showing compositions between Fo_{82-77} . Kituharu tephra also has unzoned olivine and olivine with subtle “shoulder” profiles at $\sim Fo_{85.5}$, which falls within the rim compositions of zoned crystals. The NE Tephra sample has one complexly zoned olivine, which exhibits a Fo_{80} core which grades into a step at Fo_{72} , and a thin, 25 μm rim at Fo_{79} . Mugara olivine are all normally zoned, but some are more subtly zoned than others (e.g. Fo_{84} core, $Fo_{83.5}$ rim). Olivine from Lac Vert show the most gradation. All olivine within a given tephra sample converge at a similar Fo composition. Rim compositions are $Fo_{85.0}$ (± 1.3 mol % Fo) at Shove, $Fo_{84.6}$ (± 1.3) at Kituharu, $Fo_{84.1}$ (± 0.8), $Fo_{83.0}$ at Nzulu (± 2), $Fo_{80.0}$ (± 2) at the NE tephra, and $Fo_{73.9}$ (± 1.4) at Lac Vert.

Minor and trace elements in olivine show interesting differences between Nyiragongo (Mugara), Nyamulagira (Nzulu, Kituharu, Shove, NE Tephra), and Lac Vert olivine. Nickel, an element that readily substitutes for Mg and Fe in olivine, reaches concentrations up to 0.35 wt% Ni, and positively correlates with olivine Fo content. Olivine from Molendijk et al. (2024; 2025) reach even higher Ni concentrations, although these high values are from the Muja picrite, which is an outlier among cones in the VVP. At lower Fo content ($<Fo_{84}$), the slope of Ni versus Forsterite becomes more gradual. At Nyiragongo, CaO concentrations in olivine are moderately higher (~ 0.5 wt % CaO) in comparison to Nyamulagira (0.38 wt % CaO). Near the olivine-glass interface, CaO concentrations reach up to 3.9 wt%, although given the high concentration of CaO in matrix glasses and the potential for secondary fluorescence effects (Gavrilenko et al., 2023), we

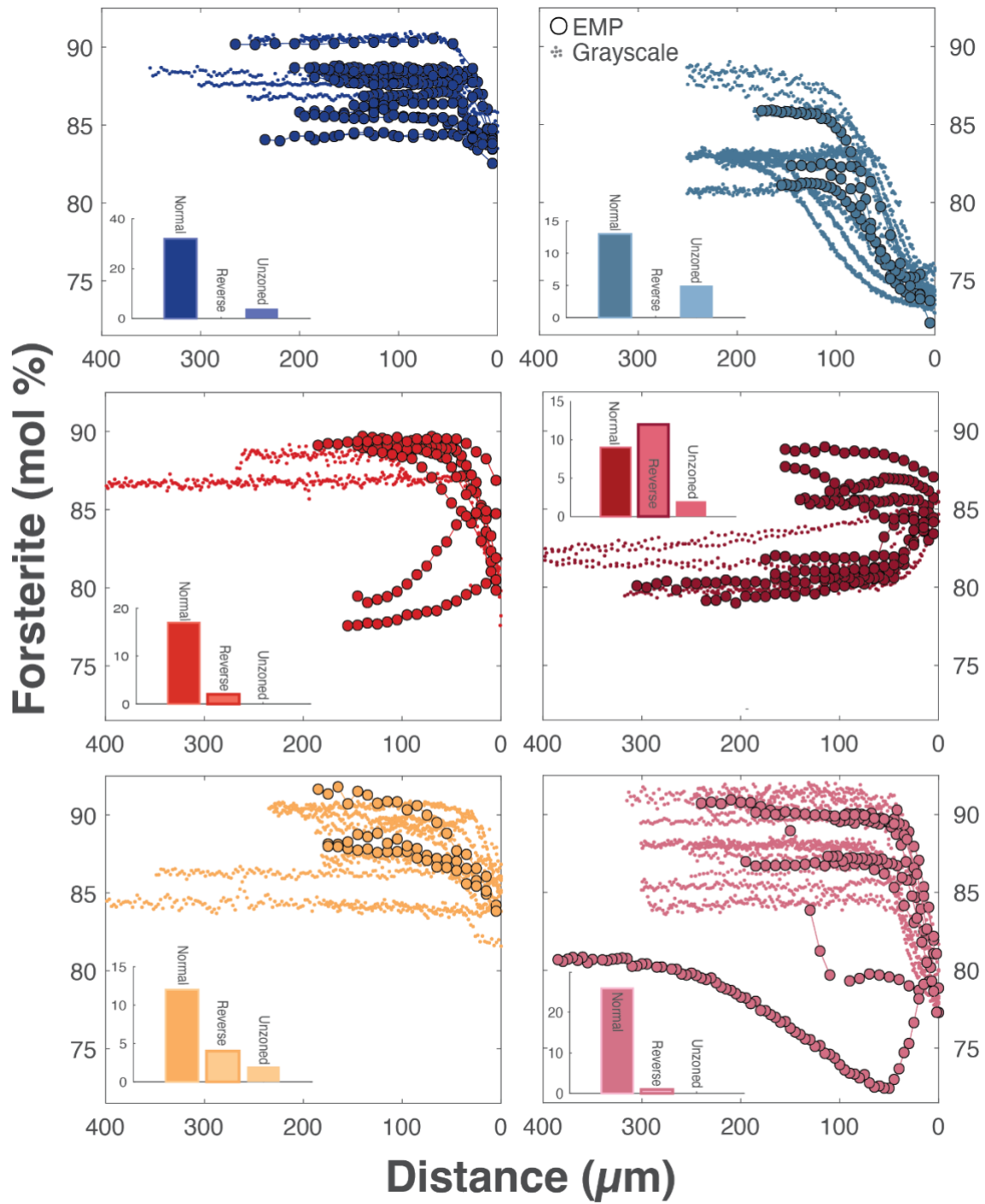


Figure 3. Plotted transects of forsterite compositions, separated by cone. Proportions of normal, reverse, and unzoned olivine are based on a larger dataset of core and rim measurements of olivine. Olivine are defined as unzoned if core and rims fall within 0.5 mol % of each other. Large markers indicate EMPA forsterite concentrations, whereas small markers indicate concentrations from BSE grayscale.

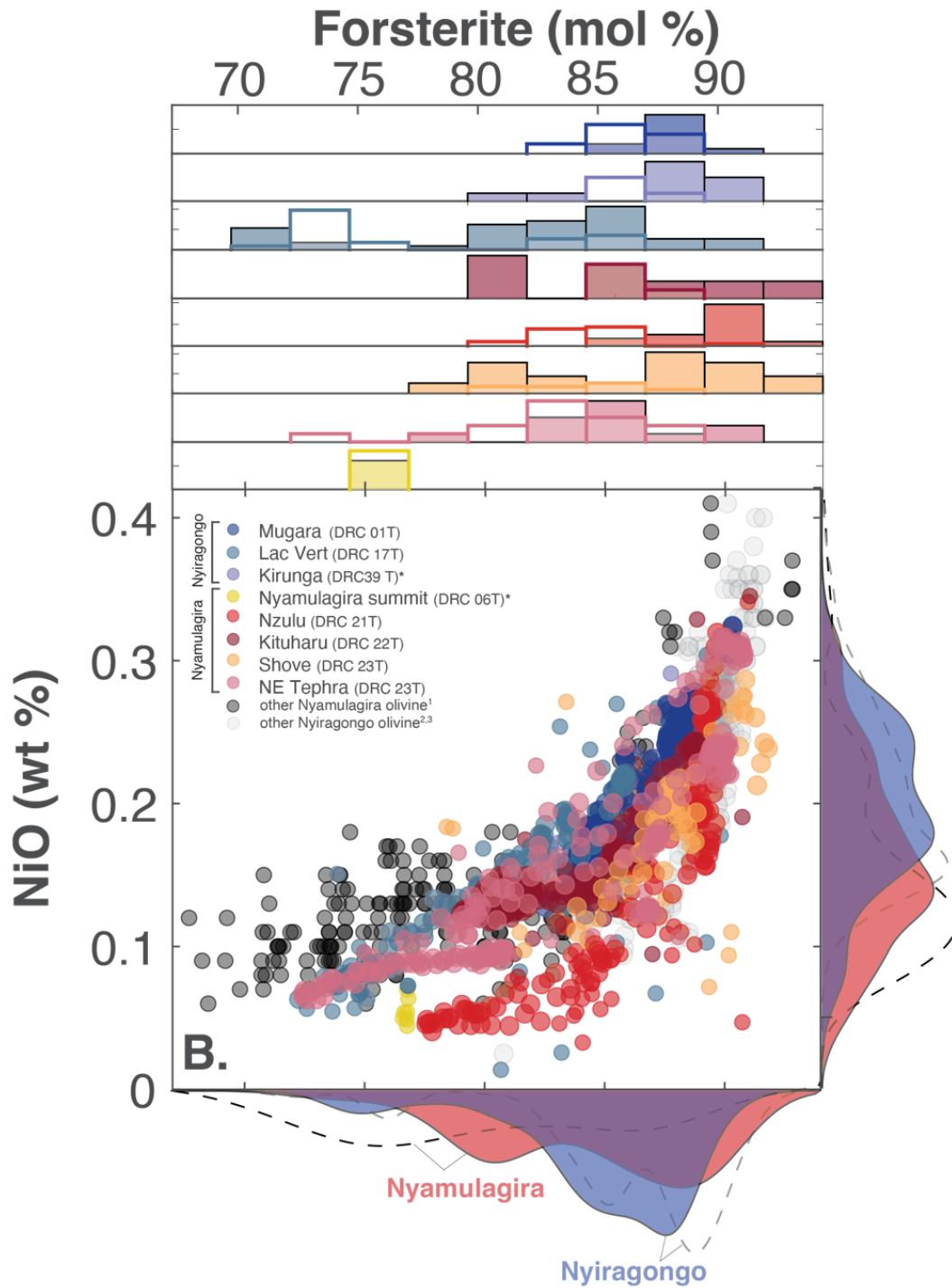


Figure 4. **A.** Histograms of olivine Fo content in tephra from this study (cores are shaded; rims are unshaded). **B.** Scatterplot of olivine Fo content versus NiO concentrations, including olivine from Nyamulagira (1: Katme Kahleghetso et al., 2025) and Nyiragongo (2: Molendijk et al., 2024; 3: Molendijk et al., 2025) lavas for comparison. Olivine from DRC06T and 39T only include core and rim measurements, and not transect data

interpret CaO contents >1.5 wt % near olivine rims to be potentially affected by secondary fluorescence, using Ca-rich olivine from Gee and Sack to inform this cutoff. Olivine compositions show negative correlations between Fo and MnO concentrations, reaching ~ 0.55 wt% MnO in evolved Lac Vert olivine. Chromium concentrations do not seem to differ among samples (~ 0.08 wt % in highest Mg olivine), and fall below detection limit at lower forsterite values. Contents of Al_2O_3 are similarly low, with higher values potentially reflecting secondary fluorescence. Lastly, most P_2O_5 values fall below detection limits, except for concentrations at the rims, which reach up to 0.1 wt %.

The MgO contents of matrix glasses adhering to olivine were previously analyzed (see Chap. 2). Matrix glass MgO contents are the highest at Shove (6.48 ± 0.5), followed by Kituharu (6.2 ± 0.5 wt % MgO), Mugara (5.8 ± 0.5 wt % MgO), Nzulu (5.2 ± 0.2 wt % MgO), Lac Vert (4.6 ± 1.4 wt % MgO), and NE Tephra (4.15 ± 0.4 wt % MgO). Matrix glasses from Lac Vert show the greatest variability, consistent with heterogeneous flow banding textures identified petrographically in this sample (Fig. S8)

5. Discussion

5.1 Assessing equilibrium

To determine whether olivine rim compositions were in equilibrium with matrix glasses upon eruption, we compare melt Mg#’s to olivine rim compositions. While partitioning relationships (K_d) of Mg and Fe between olivine and mafic melts have been rigorously investigated (Shea et al., 2022), significant uncertainty remains for the partitioning behavior in Nyiragongo’s strongly silica undersaturated compositions. Equation A2 from Matzen et al. (2011) accounts for melt composition using CMAS components and is reasonably suited to calculate K_d because it is based on a large experimental dataset including olivine melilites and nephelinites from Gee and Sack (1988). Calculations using the K_d formulation from Equation 8d in Putirka (2016) were also explored, as they also include the Gee and Sack (1988) data (Fig. S4) and yield comparable K_d values.

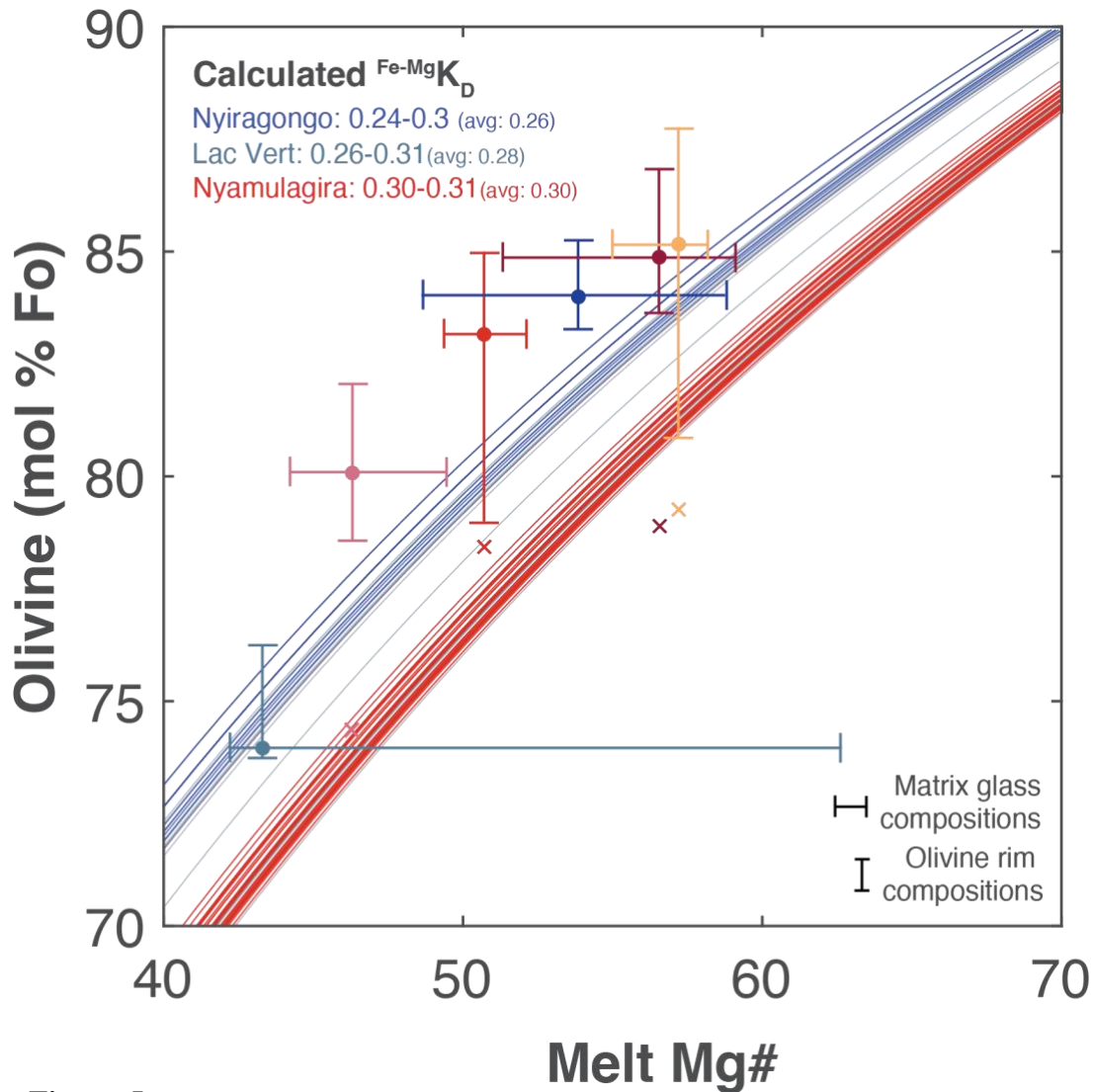


Figure 5. Average melt Mg# plotted against average olivine rim composition. Spherical markers show the average rim and average matrix glass composition. Error bars in the x direction show the range of Mg# for matrix glasses within a tephra unit. Error bars in the y-direction show the range of olivine rim compositions within the tephra unit. 'X' symbols indicate reversely zoned olivine compositions within tephra units. Gray field indicates calculated K_d values from Matzen et al. (2011).

Using matrix glass compositions and olivine, calculated K_d values range from 0.24-0.31, where K_d values for Nyiragongo are the lowest (avg: 0.26), followed by Lac Vert (avg: 0.28), followed by Nyamulagira (avg: 0.30). These range of K_d values calculated from matrix glasses are shown in Figure 5, where the x-axis shows the average and range of matrix glass Mg#s for each sample versus the average and range of olivine rim compositions on the y-axis. Comparisons between calculated equilibrium curves and measured matrix and olivine values seem to indicate disequilibrium conditions for most

olivine. Lac Vert olivine are the exception, where olivine Fo contents fall more clearly within equilibrium of average melt MgO contents, despite the presence of some high MgO matrix glasses, which suggests incomplete mixing by the time the magma had erupted. Wide ranges in matrix glass compositions may also be the effect of analytical error and/or contamination from microlite phases.

Given the systematic vertical offset of olivine forsterite contents compared to equilibrium values, it is possible that this K_d parameterization is inappropriate for the compositions here. Support for equilibrium between olivine rims and matrix glass comes from the relations in Figure 3, where olivine rim compositions in a given sample approach a common value. Examining the compositions of quenched experimental glasses from Gee and Sack (1988), their olivine nephelinites and melilitites only reach ~ 4.5 wt % MgO, compared to natural matrix glasses up to 6.5 wt % in our sample suite. The Lac Vert glasses, with their low MgO contents and high alkalis, are the only compositions that fall within the compositional range of the Gee and Sack (1988) experimental glasses, and our calculated K_d values for the Lac Vert glasses successfully predict an equilibrium relationship. If matrix glasses from the other tephra samples are in equilibrium with their olivine rims, then K_d values would need to be lower by ~ 0.02 , which is well within the uncertainty of experimentally calibrated relationships. Future experimental studies on partitioning between olivine and high-Mg alkalic melts would help reconcile these uncertainties. Given these uncertainties, we cautiously interpret olivine rims to be in equilibrium with their host melts.

5.2 Identifying magmatic environments

Magmatic systems beneath large active volcanoes are dynamic, containing multiple melt reservoirs and mush zones, all with variable temperature, pressure, f_{O_2} , and composition. Tracing interactions between these multiple reservoirs is vital for understanding the paths that magmas take to the surface. Before determining timescales of magmatic processes, it is necessary to define the characteristics of individual magma reservoirs prior to mixing (e.g. Kahl et al., 2011). Primitive (Fo>85) olivine cores,

regardless of source magma, do not show significant differences in minor elements at similar Fo values. Melt inclusion geochemistry (Chap. 2), specifically SiO₂ concentrations, show subtle differences in melt composition between magma types, highlighting DRC01T [Mugara] as distinctly Nyiragongo type and other samples as dominantly Nyamulagira type.

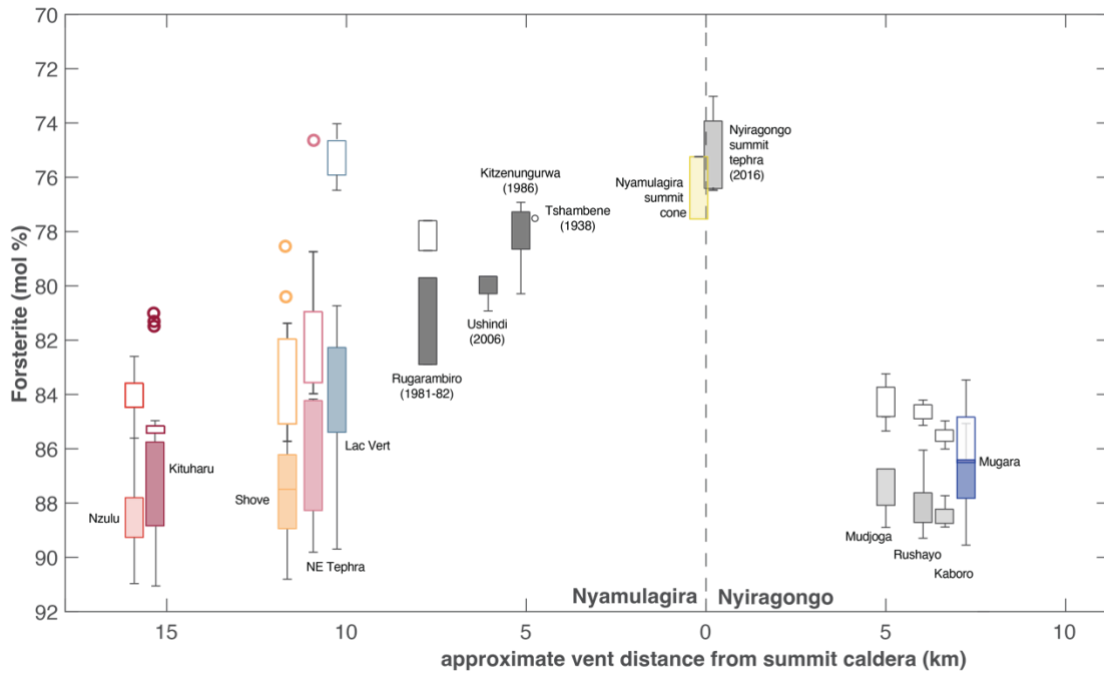


Figure 6. Ranges of core (solid boxes) and rim (hollow boxes) contents for different eruptions at Nyiragongo (right) and Nyamulagira (left), with depth from the summit caldera plotted on the x-axis.. Hollow circles indicate outlier olivine core compositions, which exhibit reverse zonation. Comparison data for Rugarambiro from Aoki et al. (1985), Nyiragongo 2016 vent from Minissale et al. (2019), and Nyiragongo cones from Molendijk et al. (2024).

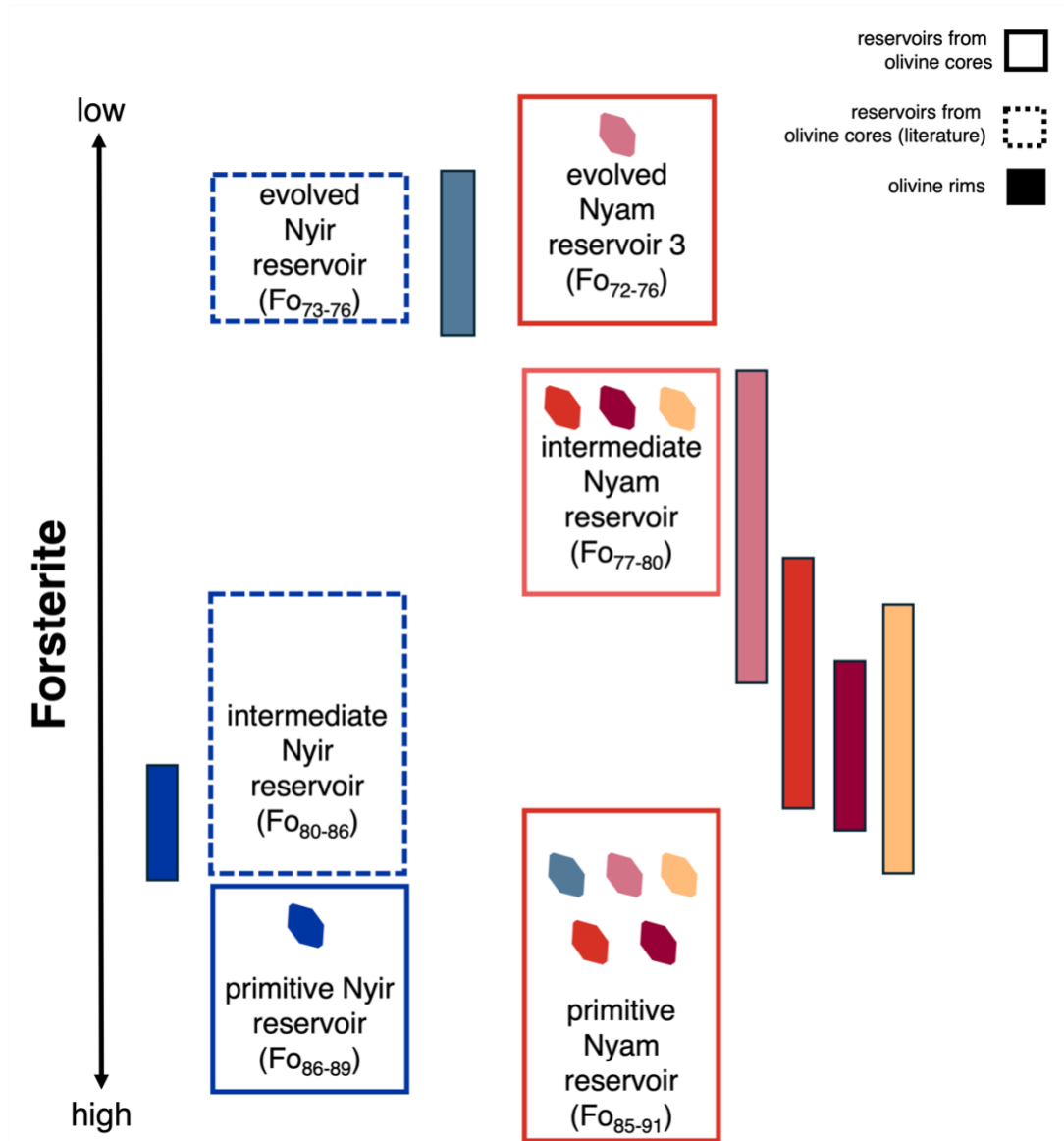


Figure 7. Schematic diagram of magma reservoirs with ranges of forsterite values based on olivine composition

Using compositions of olivine in this study and in the literature, we define end members of primitive, intermediate, and evolved reservoirs (Fig. 6; Fig. 7). Melt inclusions and clinopyroxene barometry at Nyiragongo and Nyamulagira (Molendijk et al., 2024; Katme Kaleghetso et al., 2025; Connors et al., *in review*) show that primitive, Mg-rich magmas tend to be stored at greater depths than evolved magmas. Normally zoned olivine

cores from Mugara (Fo₈₆₋₈₉) define Nyiragongo's primitive reservoir. This range in core compositions is similar to olivine from other Nyiragongo flank cones (Molendijk et al., 2024). Physically, the inferred storage reservoirs could represent either separate smaller plumbing systems beneath the distal flank vents, or they could be parts of the deeper and larger plumbing system beneath Nyiragongo, wherein the earliest stages of primitive magma crystallization occur (R3 of Pouclet and Bram, 2021), and which feed flank vents via lateral flow from depth. In the absence of intermediate olivine cores in our dataset, we define an intermediate reservoir (inferred to be slightly shallower) using core compositions (Fo_{~80-86}) from olivine basalts from Molendijk et al. (2024). Using olivine Fo content from recent summit-sourced eruptions of Nyiragongo in 2002, 2016, and 2021 (Fo₇₃₋₇₆; Minissale et al 2019; Minissale et al. 2022; Molendijk et al., 2024), we define Nyiragongo's evolved reservoir, which supplies summit lava lake activity (equivalent to R2 of Pouclet and Bram 2021). Much smaller and more spatially discontinuous reservoirs with similarly evolved compositions may also be present beneath flank regions. Primitive melt inclusions from DRC17T, 21T, 22T, 23T, and 31T all have compositions like Nyamulagira. Normally zoned cores (Fo₈₅₋₉₁) from these samples all cover the same range of Fo values which we designate as the deep Nyamulagira reservoir. It is possible that within the range of olivine grouped here there are multiple distinctly identifiable reservoirs, but this entire range of olivine compositions falls within a similar range defined as olivine population 1 (Fo₈₆₋₉₂) from Katme Kaleghetso et al. (2025). Olivine from Nyamulagira's 1981-1982 Rugarambiro eruption also fall between Fo₈₆ and Fo₈₈ (Aoki et al., 1985). Cores of reversely zoned crystals from DRC21T, 22, 23, and 31 (core Fo values Fo₇₇₋₈₀) constitute the intermediate reservoir. Forsterite concentrations here align well with olivine cores (Fo₇₇₋₈₀) found from 1986 and 2006 tephra (Head et al., 2011) erupted near the summit and a population of olivine from the 1981-82 Rugarambiro eruption (Aoki et al. 1985). More evolved Fo₇₂₋₇₆ olivine from the Nyamulagira summit cone represent Nyamulagira's evolved reservoir. The presence of similar compositions in the core of the complexly zoned NE Tephra olivine (Fig. 4), far from Nyamulagira summit, suggest again that evolved magma may be present in other smaller, shallow dispersed reservoirs. Tephrites from Katme Kaleghetso et al. (2025) extend to even more evolved olivine (Fo₆₈).

Rim compositions of olivine from our dataset provide clues as to what reservoirs mix with one another. Olivine rim data show that primitive reservoirs mix with more intermediate reservoirs prior to eruption. At Nyamulagira specifically, olivine rims from 21T, 21T, and 23T (Fo₇₈₋₈₆) seem to equilibrate with a magma between the intermediate and evolved reservoirs, suggesting either the existence of another reservoir between these, or that the intermediate reservoir has experienced compositional variations throughout its history. In comparison, magma from the 31T [NE Tephra] equilibrated with a composition fitting more within the intermediate reservoir. Olivine with an Fo₇₂ core from this sample is likely xenocrystic, but may represent shallowly-sourced olivine transported to intermediate depths, and laterally transported away from the reservoir as suggested by numerical models (Walwer et al., 2023).

Differences in reservoir interactions may explain why NE tephra olivine rims show differing growth habits than others (Fig S6). This cellular texture falling between tabular and skeletal habits implies growth rates somewhere between moderate and fast. An experimental study from Laumonier et al. (2019) suggests that low degrees of undercooling may generate cellular textures, but this would be inconsistent with the larger degrees of undercooling caused by the intrusion of NE tephra magmas into a more evolved reservoir. Olivine from this sample highlight the variability in crystal growth that can occur in a single phenocryst (Fig. S6d), where some parts of the crystal show a thick (>20 μm) rim, whereas other regions show no growth at all. These textures suggest the extent of growth is influenced by localized temperature gradients.

Lastly, rim compositions from Lac Vert (Fo₇₂₋₇₅) indicate equilibration with evolved reservoirs. Melt inclusions from evolved olivine in this sample (Fig. 2) show alkali concentrations more evolved than Nyamulagira lava lake samples, but silica-concentrations higher than Nyiragongo lava lake samples. These incongruencies suggest that the evolved reservoir in this location is a distinct magma batch independent of the two major edifices.

5.3 Diffusion modeling

Accurate constraints on model inputs are vital for diffusion modeling. For pressures, we used values calculated from volatile concentrations in melt inclusions (MI) in these same samples (Chap. 2). For DRC01 [Mugara], DRC21T [Nzulu], DRC22T [Kituharu], DRC23T [Shove] and DRC31T [NE tephra outcrop], we use 400 MPa (~14 km), approximately the median value of primitive MI from these tephra samples. For Lac Vert, we use a pressure of 100 MPa, corresponding with volatile saturation depths of the most evolved MI. For f_{O_2} , we use estimates from MI as well, based on XANES spectroscopic analyses of Fe and S (Chap. 2), yielding median primitive MI values of QFM+0.4 and evolved MI values of QFM-0.5.

Temperature has the largest effect on the magnitude of diffusion coefficients (Dohmen and Chakraborty, 2007), making accurate temperature estimates vital for calculating accurate timescales. To estimate temperatures, we developed a relationship between olivine rim composition and melt temperature, assuming equilibrium between the melt and olivine rim. We compiled a dataset of whole-rock compositions from Nyiragongo and Nyamulagira (Aoki et al., 1983; Aoki et al., 1985; Chakrabarti et al., 2009; Head et al. 2011; Phillips, 2015; Pouclet 2016; Minissale et al., 2019; Molenidjk et al. 2023; Molendijk et al., 2024; Connors et al., 2025), and used major element concentrations to calculate equilibrium olivine forsterite contents using equations A2 from Matzen et al. (2011) and Equation 8d from Putirka (2016). Both formulations yield similar equilibrium olivine values (Fig. S4a-b), but we ultimately chose the Matzen et al. (2011) formulation for our calculations. Using these calculated olivine Fo contents, we apply an olivine thermometer from Equation 22 of Putirka et al. (2008). Then, with this relationship between olivine Fo and temperature, we fit a linear relationship between temperature and olivine Fo values at Nyiragongo and Nyamualgira (Fig S4c-d). For our model temperatures, we use the average rim composition of olivine from each tephra unit (Table 1.) to calculate temperatures, which range from 1159-1208°C for primitive samples and 1024°C for evolved Lac Vert samples. The standard deviation from the olivine rim composition of each population ranges from ± 11 to 20°C. The uncertainty associated with the thermometer itself from Putirka (2008) is $\pm 29^\circ\text{C}$, propagating to an average uncertainty of $\pm 32^\circ\text{C}$.

Table 1. Initial conditions for diffusion models

Tephra	Model pressure (MPa)	Model fO_2 (ΔQFM)	Average rim composition (mol% Fo)	Rim σ (mol% Fo)	Model temperature (°C)	temperature uncertainty (°C)
Mugara (DRC01T)	450	QFM	84.1	0.8	1160	11
Lac Vert (DRC17T)	100	QFM-1	73.9	1.4	1024	18
Nzulu (DRC21T)	450	QFM	83.0	2	1189	19
Kituharu (DRC22T)	450	QFM	84.6	1.3	1204	12
Shove (DRC23T)	450	QFM	85.0	1.3	1208	20
NE Tephra (DRC31T)	450	QFM	80.0	2	1159	14

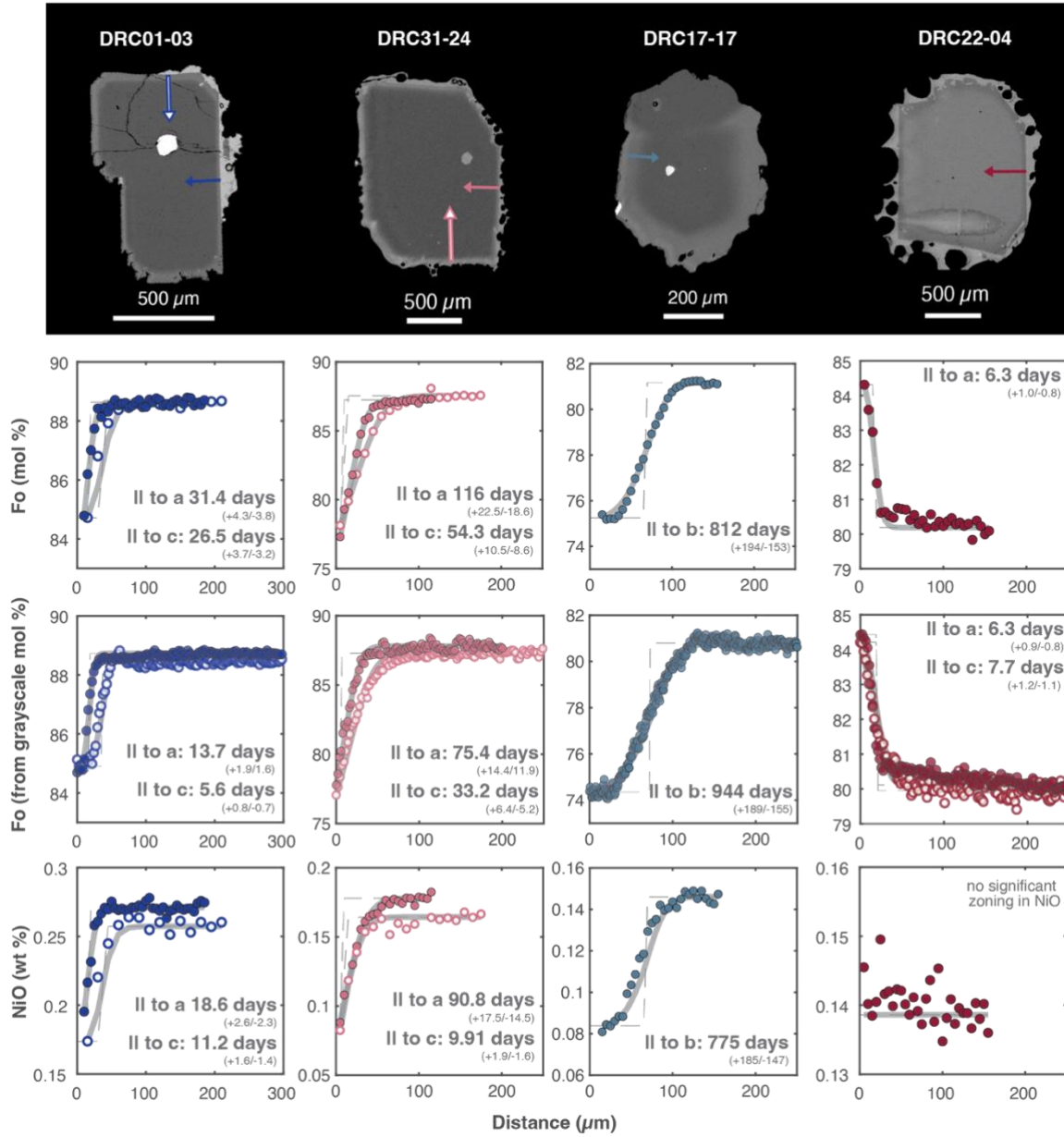


Figure 8. Best fit models of EPMA-measured olivine Fo and NiO contents (filled symbols). Also shown are olivine Fo values calculated from grayscale variations as described in the text (open symbols). Filled markers indicate transects taken along the a-axis, whereas white markers indicate transects along the c-axis. Dotted lines show initial step function compositional changes determined by best fitting models. Gray solid curves indicate best fit diffusion models.

In the practice of diffusion modeling, significant debate exists over whether measured compositional profiles are caused by diffusion alone or by rapid growth of a rim followed by diffusive relaxation of an initial step-function concentration change. In all our models, we assume stepwise zoning patterns in the outer rim are initially produced by an episode of growth. Systematics of olivine Fo and Ni can also be used to distinguish between these processes. Moderately lower diffusivities of Ni in comparison to Fo (Gordeychik et al., 2020) generate a concave upward trend during growth, whereas purely diffusion driven variability is shown through linear trends. We differentiate diffusion-driven and growth-driven variability by examining trends on a sample-by-sample basis (Fig. S7). Our model assumes that rim growth was instantaneous, but future modeling with a moving boundary condition could yield more accurate timescales. An in-situ study of olivine growth in tholeiitic melts shows that crystals can reach millimeter sizes within minutes, growing at velocities between 10^{-9} and 10^{-7} m/s depending on the axis (Welsch et al., 2024). Given the differences in composition, we cannot directly apply quantitative estimates of the timing of crystal growth, but can to a first order suggest that olivine rim crystallization occurred relatively rapidly based on the narrowness of the rims and textural features on the rims noted previously. Experimental studies, also done on tholeiitic melts, suggest that rapid growth following a single burst of nucleation does not produce the gradational zoning frequently observed in olivine compositional profiles (Shea et al. 2022).

In total, 41 transects of measured olivine Fo content and Ni and 83 grayscale transects were used in estimating magma mixing-to-eruption timescales based on zoned olivine rims (Fig 7). Timescales estimated for transects on the same grain taken in different directions are roughly comparable to one another, although timescales calculated from measurements in the a and b directions tend to be faster (Fig. S9a). Uncertainties still exist regarding the degree of anisotropy, and it is possible that the difference in diffusion coefficients is not as high (4x faster on c compared to a and b instead of 6; Chakraborty, 2010). When compiling results, we consider the timescale of grains with multiple transects as an average between the two values. In comparing Fo versus Ni-derived timescales, two populations can be identified. Most of the olivine show systematically shorter Ni timescales than Fo (Fig. S9b), something that has also been identified at other systems

(Lynn et al. 2017; Ruth et al. 2018; Mourey et al., 2023), and attributed to lower levels of accuracy in the diffusion coefficient of Ni (Gordeychik et al., 2020). Olivine with higher Ni timescales come from samples with relatively subtler Ni zoning, which may result in longer timescales as an artifact of data fitting. When computing average timescales for tephra units, we removed timescales calculated from grains where no significant Ni zonation was present (n=2). Timescales calculated from grayscale values show systematically shorter timescales compared to those calculated from measured EPMA analyses. We interpret these shorter timescales as a result of the higher spatial resolution of grayscale-estimated compositions close to the olivine-melt interface. To avoid contamination from the high Ca, Na, and K of the matrix glasses, rim analyses of olivine needed to be $\sim 10\ \mu\text{m}$ away from the interface. With grayscale analyses in ImageJ, concentrations can be estimated within $1\ \mu\text{m}$ of the boundary. This increased spatial precision better aided the assignment of step function locations, ultimately leading to faster timescales, with timescales reducing on average by 50%. For normally and reversely zoned crystals, we find no significant difference between modeled timescales, supporting the idea that for tephra with mixed crystal populations, all crystals equilibrated in the same mixed melt environment.

Modeled timescales for the different tephra units (Table 2; Fig. 8) fall into two groups. The longest timescales come from the DRC17T [Lac Vert] olivine, which show compositional gradients >100 microns in length, yielding timescales ranging from ~ 9 months to 4.5 years. For all other olivine, timescales are significantly shorter, with median timescales ranging from 14.1-31.8 days.

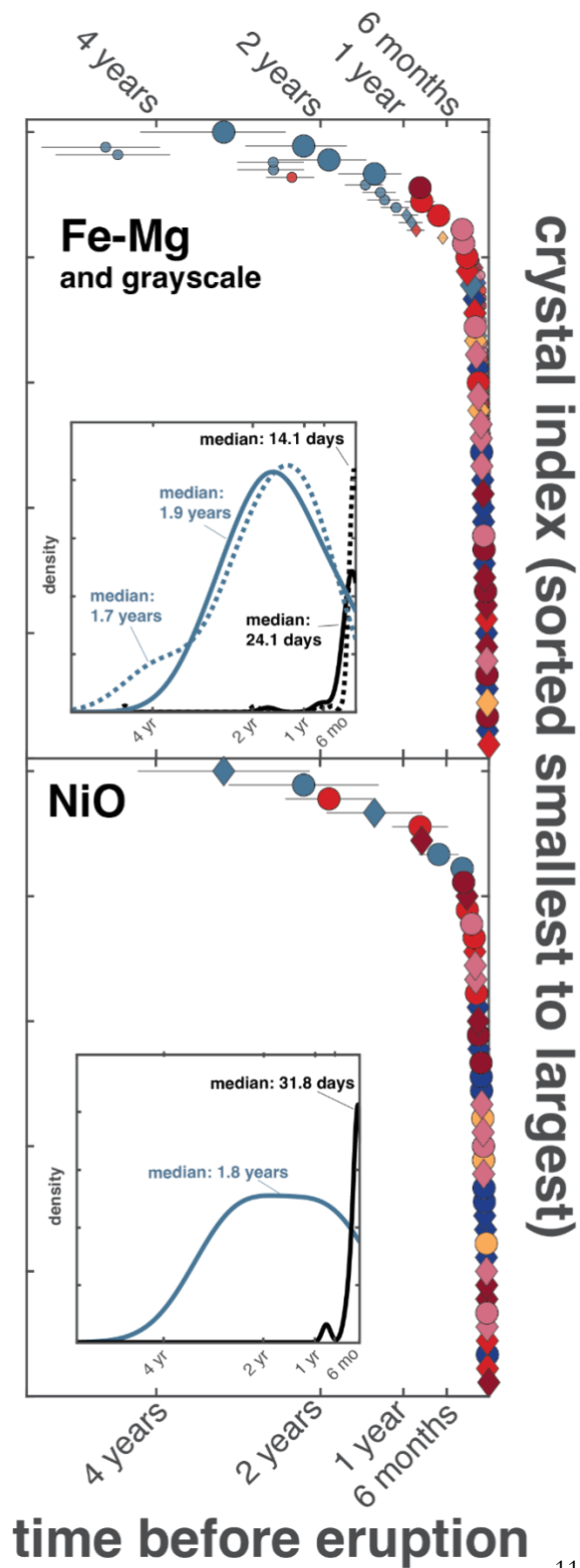


Figure 9. A. Timescales from Fe-Mg diffusion model results from measured (solid curve) and grayscale inferred (dotted) composition profiles, with medians at 1.9 and 1.7 years, respectively, for Lac Vert samples, and 24.1 and 14.1 days, respectively, for all other samples. B. Timescales from NiO diffusion, with a median at 1.8 years for Lac Vert samples and 31.8 days for all other samples.

Table 2. Average timescales (excluding outliers) for tephra units

Tephra	Average Fe-Mg timescale	Average Ni timescale	Average grayscale timescale
Mugara (DRC01T)	24 (days)	25 (days)	10 (days)
Lac Vert (DRC17T)	1.7 (years)	1.8 (years)	2 (years)
Nzulu (DRC21T)	49 (days)	43 (days)	17 (days)
Kituharu (DRC22T)	45 (days)	34 (days)	16 (days)
Shove (DRC23T)	31 (days)	24 (days)	26 (days)
NE Tephra (DRC31T)	48 (days)	32 (days)	24 (days)

While the same diffusion coefficient formulations are used in most diffusion modeling studies, recent experimental results cast doubt on rates of cation diffusion. Most diffusion coefficients have been determined by measuring compositional gradients across solid-solid couples of oxides at high temperatures. In contrast, diffusion coefficients extracted from experiments conducted in a silicate melt environment (Jurewicz and Watson 1988; Spandler and O’Neil, 2010; Shea et al., 2023) all have yielded significantly faster rates, with most recent experiments from Shea et al. (2023) yielding diffusivities up to ten times higher than those from solid-solid couples. The precise causes of these discrepancies in results remain unclear, but one hypothesis involves the presence of H, Al, Ti, and Na in the melt, which may facilitate the formation of point defects near the melt-olivine interface. With this in mind, we calculated the effect of faster diffusivities on our modeled timescales (Fig. 10). For Lac Vert olivine, the median timescale decreases from 1.9 years to 2.4 months. For primitive olivine in all other tephra samples, the median timescale decreases from 24 days to 2.4 days. At other volcanic systems, higher diffusivities yield timescales that contradict the apparent consistency of diffusion timescales and monitoring signals of

unrest. We discuss our timescales in comparison with the monitoring record in the section below on “Comparisons to active monitoring”.

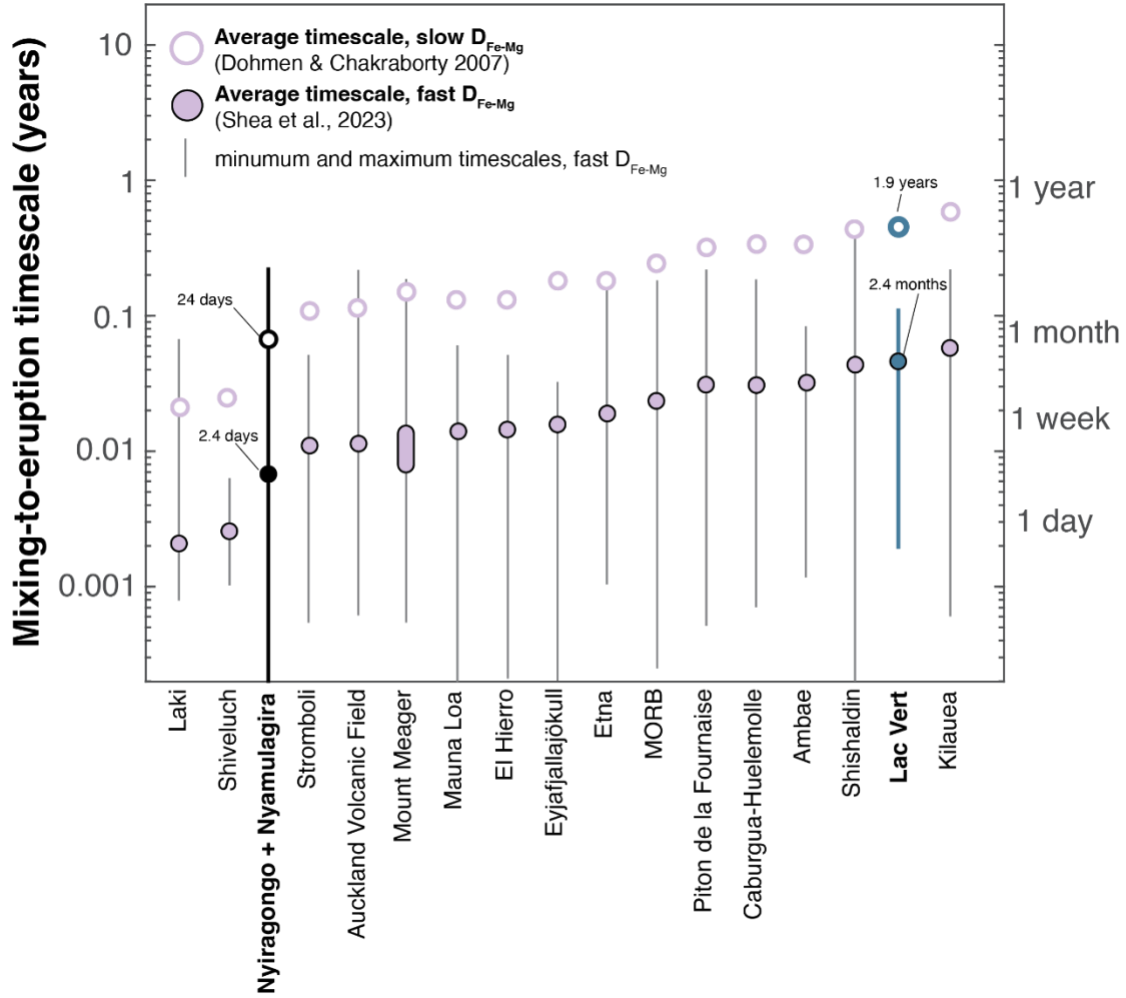


Figure 10. Compilation of magma mixing-to-eruption timescales from Fe-Mg diffusion chronometry in olivine from mafic eruptions, compared with Nyiragongo and Nyamulagira results. Open circles represent average mixing-to-eruption timescales using D_{Fe-Mg} calculated with the Dohmen and Chakraborty (2007) D_{Fe-Mg} . Filled circles represent timescales calculated with the $\sim 10\times$ faster D_{Fe-Mg} from Shea et al. (2023). Lac Vert timescales are shown separately because they are significantly longer than the other cones in our study. Compiled timescales here come from Shea et al. (2023), with the addition of timescale from Mt. Meager (Aufrere et al., 2024).

5.4 Decompression and ascent rates of magma during eruption

To model timescales of decompression in ascending magmas during eruption, we use a recently published olivine-melt K_d value for H_2O of 0.0009 (± 0.0003) from Towbin et al. (2023), which is lower than previously determined K_d estimates (e.g. Hauri et al. 2006). We calculated diffusion coefficients for H^+ in olivine parallel to the a-direction using an Arrhenius relationship from Barth et al. (2019) at temperatures between 1160 and 1208°C (corresponding to temperatures of rims). The transect in Figure 11 was taken parallel to the a- direction, which is slower than diffusion along the c-direction (Ferriss et al., 2018). In the models, we vary K_d between 0.0007 and 0.0011. All models were run for 1000 iterations, and decompression results are expressed as mean values with uncertainties

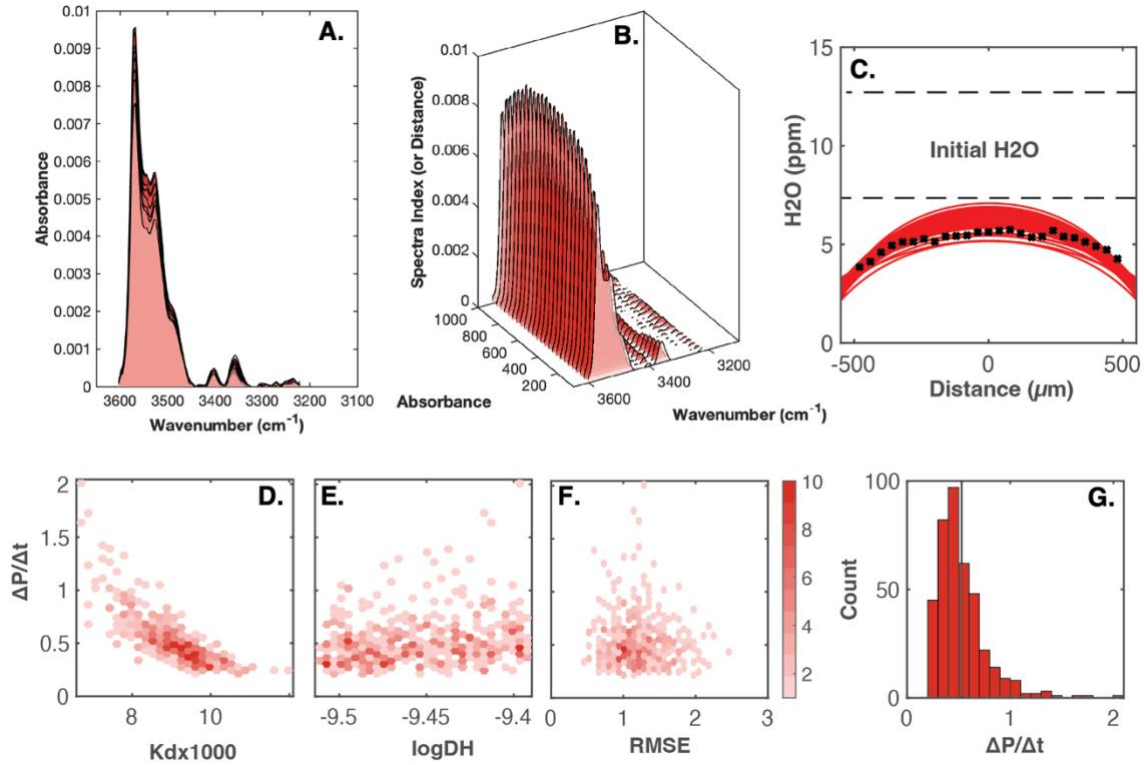


Figure 11. A. IR spectra of olivine, with stretching regions associated with H^+ shown. Shades of red indicate the total integrated absorbance (red = high, pink = low). B. IR spectra across same transect as in panel A, with distance on the z-axis. C. Diffusion model of H^+ in olivine, with ranges of initial H_2O contents indicated by dotted lines. D. Plotted decompression timescales against estimated K_d values. E. Plotted decompression timescales against diffusion coefficients. F. Plotted decompression timescales against misfit (expressed as root mean square error). G. Histogram of decompression timescales.

expressed as standard deviations (Fig. 11). Resulting decompression rates negatively correlate with K_d in our specified range (Fig. 11d). Calculated root mean square errors show the lowest misfit values at decompression rates of <0.5 MPa/s.

If we assume olivine is recording ascent from an intermediate reservoir ~ 10 km below the surface of the vent (~ 280 MPa), then this corresponds to an ascent rate of $\sim 18 \pm 9$ m/s, equivalent to estimates of ascent for the primitive 3930 BP eruption of Mt. Etna (Barth et al., 2024). This is faster than the VEI 3 explosive basaltic eruptions of 1992 at Cerro Negro (0.007 MPa/s; Barth et al., 2019) and Segoum volcano (0.07 MPa/s; Newcombe et al. (2020)).

5.5 Comparisons to active monitoring

In the region, monitoring efforts have been historically inhibited by geopolitical unrest. While a regional 5-station seismic network was installed in 1994, multiple stations were damaged, and many observations rely on only 2-stations, reducing accuracy in observations. In 2013, a regional broadband seismic network was constructed (KivuSNet: Oth et al., 2013) and has greatly improved data quality. Additionally, a 15-station GPS network (KivuGNet) came online in 2009 (Geirsson et al., 2017). Deformation at Nyamulagira and Nyiragongo has been monitored remotely via InSAR since 2005 (d'Oreye et al., 2008; Wauthier et al., 2015). Numerous field campaigns have investigated degassing processes at both volcanoes (Sawyer et al., 2008, Bobrowski et al. 2017a; Bobrowski et al., 2017b; Barriere et al. 2022; Boudoire et al., 2022), and MultiGAS instrumentation has been deployed at the Nyiragongo summit (Balagizi et al., 2023).

The 2010 eruption of Nyamulagira has the most continuous, multi-method record of seismicity, degassing, and ground deformation (Smets et al., 2014). While a major goal of diffusion chronometry is to draw parallels between diffusive equilibration timescales and monitoring signals, these connections are most robustly drawn between modern monitoring signals and their eruptive products. In this section, we assess whether any

modern eruptions serve as appropriate analogues for timescales modeled in prehistoric eruptions reported here.

For Nyiragongo, historically observed eruptions all involve the shallow, evolved summit reservoir. In advance of both the 1977 and 2002 eruptions, lava lake level fluctuation and intense degassing activity were observed for 6 months (Pottier, 1978; Komorowski et al., 2002), and are interpreted to represent precursory signals. The existence of precursors to the deadly 2021 eruption remains debated, where one analysis of multidisciplinary monitoring data asserted no precursors (Smittarello et al., 2022), but another analysis noted subtle precursory seismicity weeks prior (Kyambikwa et al., 2024). Regardless, teasing precursory signals is challenging at open-vent systems, as not all seismic events lead to eruption (e.g. Barriere et al., 2022), and persistent degassing can obfuscate signs of deep magma transport (Acoella et al., 2023). While the 2021 eruption was likely triggered by edifice rupture (Burgi et al., 2020; Smittarello et al., 2022), high Fo olivine found in erupted lavas indicates the involvement of deeper primitive reservoirs.

Since 1882, Nyamulagira has experienced at least 42 eruptions (Smets et al., 2015), with precursory seismic signals first noted preceding the 1912 eruption of Rumoka (Global Volcanism Program). For eruptions between 1971 and 1981 (Pouclet and Villanueva, 1972; Tanaka et al., 1982), precursory seismicity seems to have occurred hours before the eruption. It is difficult however to determine whether subtler signals occurred but were not identifiable given instrumentation capabilities. The highest resolution monitoring dataset prior to an eruption at Nyamulagira comes from the 2010 eruption (Smets et al., 2014), in which seismicity, ground deformation, and SO₂ degassing all increased over 3-4 weeks before the eruption.

When considering the compositions of eruptive products, modern eruptions from both volcanoes have been relatively evolved in composition. At Nyamulagira, analyses of lavas since 1938 show relatively consistent MgO contents (4.2-6.5 wt % MgO; Head et al., 2011; Smets et al., 2015; Pouclet and Bram, 2021; Katme Kaleghetso et al., 2025), and eruptions have dominantly occurred in the near summit region. Depth estimates from recent eruptions (Head et al., 2011; Katme Kahleghetso et al., 2025; Connors et al., 2025) suggest

recently erupted, near summit, evolved magmas are dominantly tapped from a shallower reservoir. Geophysical modeling of deformation prior to the 2010 eruption (Wauthier et al., 2015) aligns with this interpretation, suggesting the tapping of a shallow reservoir ~3.5 km below the summit. These lines of evidence suggest a relatively steady state of eruptions and their sources over the past 100 years. It should be noted, however, that these interpretations rely on relatively sparse numbers of samples from large volumes of lava, which have the capacity to be heterogeneous on various spatial scales. Additionally, analyses of the 1954 Mihaga eruption, which included both caldera activity and vent opening ~6.6 km from the summit caldera, erupted tephra with ~8.5 wt% MgO and olivine up to Fo₈₉ (Katme Kahlegetso et al., 2025). While closer in composition to tephra from this study (MgO 10.9-14.3 wt %), this is still a questionably analogue to the flank eruptions that we studied, given its proximity to the summit caldera. The most recent eruption with high enough MgO contents would be the 1912 Rumoka eruption. In a recent review from Pouclet and Bram (2021), temporal trends in major element composition are used to argue for four sequences of shallow reservoir emptying and recharge since 1938. It remains unclear however whether the shallow reservoir was invaded by input from the intermediate or deep reservoir.

The unique magma compositions of DRC17T [tephra collected near Lac Vert] remain enigmatic, showing SiO₂ too high for evolved Nyiragongo compositions, and Na₂O+K₂O too high for Nyamulagira compositions. Either this batch of magma was independent of both systems, or it formed as a mixed magma with variable contributions of both magma types. Regardless, the months to years recorded by olivine timescales may be analogous to ~1 year of pre-eruptive seismicity prior to recent eruptions at Nyamulagira (Mavonga, 2010). Alternatively, if faster diffusivities are appropriate, then analogues can be found in the 2010 eruption of Nyamulagira (Smets et al., 2014). Ultimately, more diffusion studies of olivine from summit and near summit eruptions of both volcanoes would be helpful for assessing possible connections between flank eruptions and the central plumbing systems.

While some historic eruptions may be analogous to Holocene flank eruptions studied here (e.g. Mihaga, Rumoka), these eruptions lack adequate monitoring records necessary for comparison with diffusion timescales. Modern eruptions are evolved and seem to be most influenced by shallow reservoirs. The timescales modeled here based on zoned rims of olivine may provide insights into the signals preceding future primitive eruptions flank, but our results should be interpreted with caution given current uncertainties in diffusion coefficients (Shea et al., 2023). Further experimental and analytical studies are required to resolve these issues.

6. Conclusion

Major, minor, and volatile elements in the mineral olivine can record processes on multiple timescales. When coupled with experimentally derived diffusivities, these concentrations provide useful insights into timescales between magma mixing and eruption, and timescales of magma ascent. Zoning patterns in 83 olivine phenocrysts across 5 tephra forming eruptions at the flanks of Nyiragongo and Nyamulagira provide the first estimates of pre-eruptive timescales at both volcanoes.

Combining our data with published data for olivine compositions from both historic and pre-historic eruptions, we construct a model to define magmatic environments of olivine crystallization at both Nyiragongo and Nyamulagira. With these results, we estimate the pressure, temperature and f_{O_2} conditions of magma storage. Using modeling of core to rim forsterite contents (both measured and calculated through grayscale values) and Ni concentrations, we estimate timescales between magma mixing and eruption, which range from 14.1 to 31.8 days for primitive olivine from the 01T [Mugara], 21T [Nzulu], 22T [Kituharu], 23T [Shove], and 31T [NE tephra cones]. For more evolved olivine from Lac Vert, we estimate timescales between 9 months and 4.5 years. Estimates of ascent rate from an H^+ traverses in olivine suggest decompression timescales <0.5 MPa/s, corresponding to ascent rates of ~ 18 m/s. Our results indicate magma decompression rates during eruption at the fast end of other eruptions that have been investigated with this method, and such rates seem to be common to other relatively explosive mafic eruptions

(Barth et al., 2024). When contextualizing timescales obtained from primitive eruptions at these volcanoes, analogous primitive distal eruptions lack monitoring data, despite frequent eruptions from both systems. Regardless, estimates of mixing and ascent timescales from these eruptions provide helpful insight as to how a future distal flank eruption may compare with modern activity. Future studies in this region will make diffusion constraints more robust and will improve our ability to compare monitoring signals with magmatic processes.

CHAPTER VI: DISSERTATION SUMMARY

In the field of volcanology, so many questions exist regarding the fundamental inner-workings of magmas. While a question such as “how deep is magma stored?” may seem simple, arriving at a robust answer is much more complicated. Through geochemistry, the signatures associated with pressure, temperature, or compositional conditions of magmatic environments can be estimated, but there are complications along the way. In the case of Nyiragongo and Nyamulagira, collecting samples is logistically difficult. In the laboratory, analyzing exceedingly small ($<50\text{ }\mu\text{m}$) features is challenging, measuring unique geochemical concentrations (e.g. high CO_2 glasses) is analytically challenging, and lastly – applying geochemical models to systems outside of their calibrations is also challenging. Interpreting volcanic processes at data-poor regions is difficult, and while data gaps are continually narrowing, there is still much to be learned.

In my dissertation, I sought to improve constraints on large-scale processes at Nyiragongo and Nyamulagira, through small-scale features. By analyzing over 100 melt inclusions in 8 tephra-forming eruptions with multiple microanalytical techniques, I determined magmatic volatile concentrations at depth, estimated depths of magma storage, and placed constraints on mineralogy of mantle sources of magmas at both volcanoes. Moving closer to the surface, I modeled magma degassing processes, showing how ascent of evolved CO_2 -rich magma can generate surficial emissions matching CO_2/S ratios recorded in the field by volcanic gas researchers. With Chapters II and III constraining important conditions of magma storage, I used the compositions of olivine to extract a temporal perspective of magmatic processes. By measuring zoning patterns across crystals and modeling their diffusive re-equilibration times, I estimated the timescales between magma mixing and eruption for 5 tephra-forming eruptions. My modeling results showed that for primitive magmas, the timescales ranged between 14.1 and 31.8 days, and for evolved magmas, timescales were longer, ranging from 9 months to 4.5 years. Looking at even shorter timescales, I used measured concentrations of H^+ in olivine to model rates of decompression. Estimated decompression rates suggest less than 0.5 MPa/s , equivalent to

ascent rates of $<\sim 17.5$ m/s, suggesting that primitive eruptions ascend rapidly to the surface.

There is still much to learn about volcanic processes at Nyiragongo and Nyamulagira. Future studies may focus on generating high resolution petrologic characterizations of a single eruption, showing the degree of variability found in a single event. Or perhaps experimental studies on these unique compositions can generate new information about volatile solubility, diffusion rates, crystal growth, or magma sources. Furthermore, integrated petrologic and geophysical studies of modern eruptions may inform us more about past eruptions. My dissertation adds several pieces to the puzzle that is these volcanic systems, but there is yet still so much more to learn.

APPENDIX A: SUPPLEMENTARY TABLES FOR CHAPTERS II AND III

Electronic supplementary tables for chapters II and III can be accessed online at ProQuest.

APPENDIX B: SUPPLEMENTARY TABLES AND FIGURES FOR CHAPTER IV

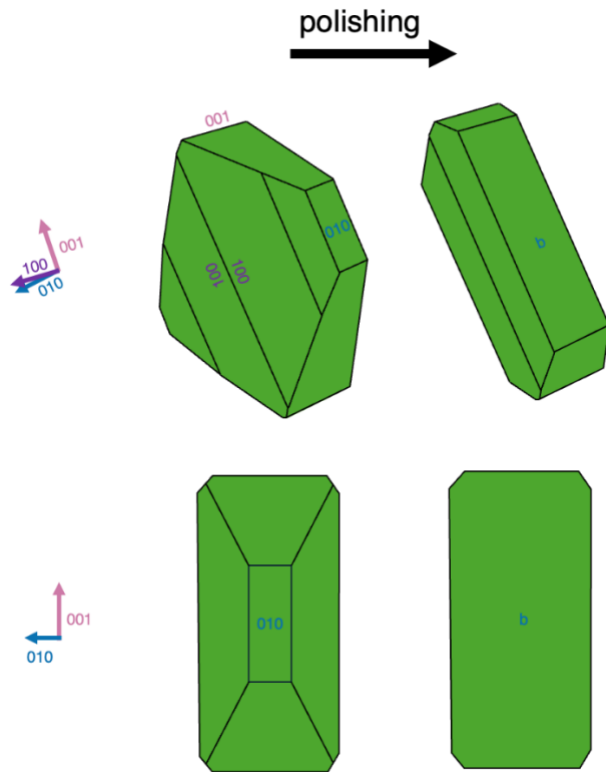


Figure S1. Polishing orientations for olivine phenocrysts perpendicular to the b-axis, shown from different 3D perspectives (modified from Lynn and DeSmither, 2023)

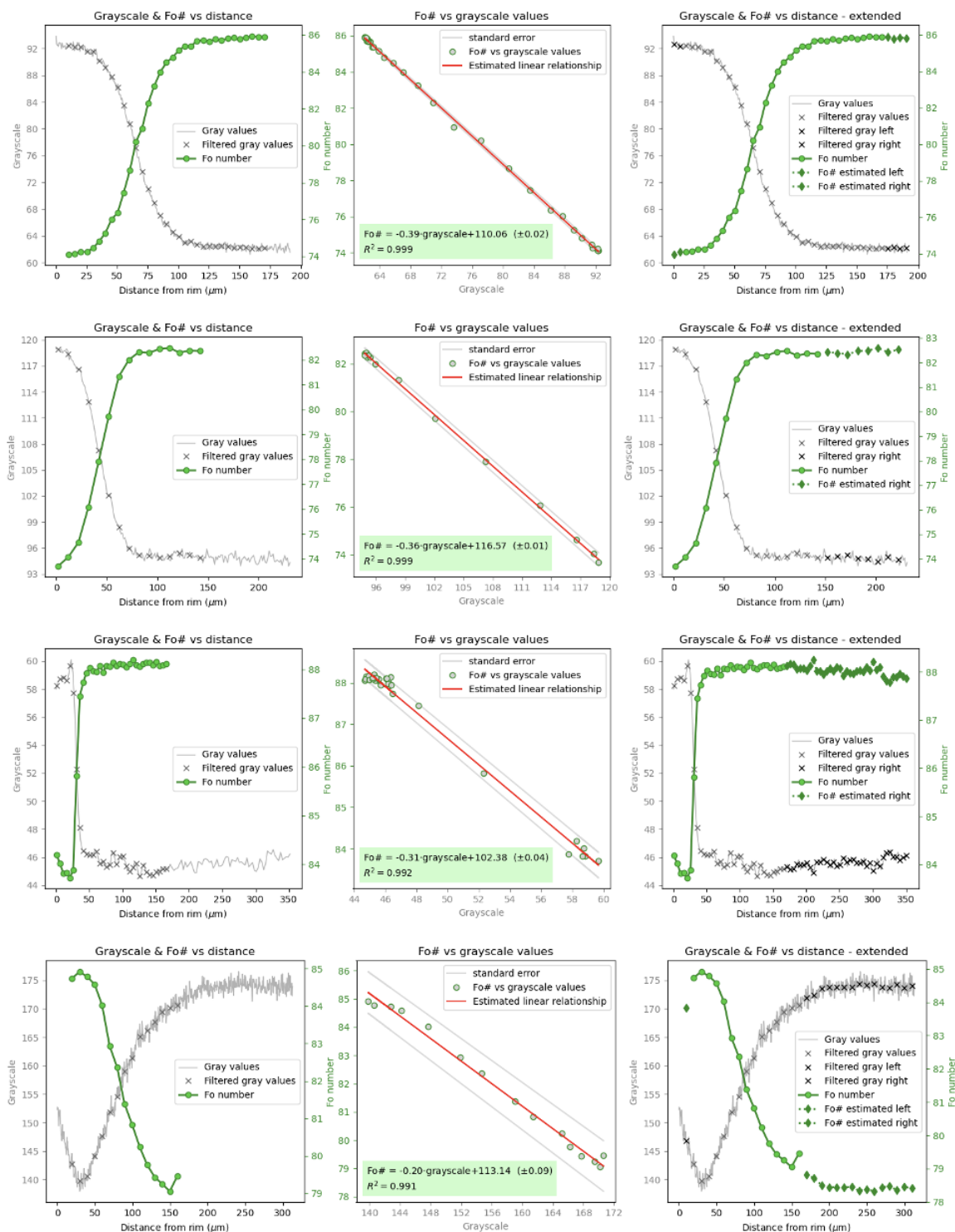


Figure S2. Four example conversions of forsterite content to grayscale content for a variety of zoning patterns. Left panels show measured forsterite and extracted grayscale values, with forsterite values plotted in green, and grayscale values plotted in gray. Red lines in middle panels show linear regressions, with standard errors plotted in gray. Left panels show the calculated forsterite values based on the linear regression, with additional data points added from the grayscale profile.

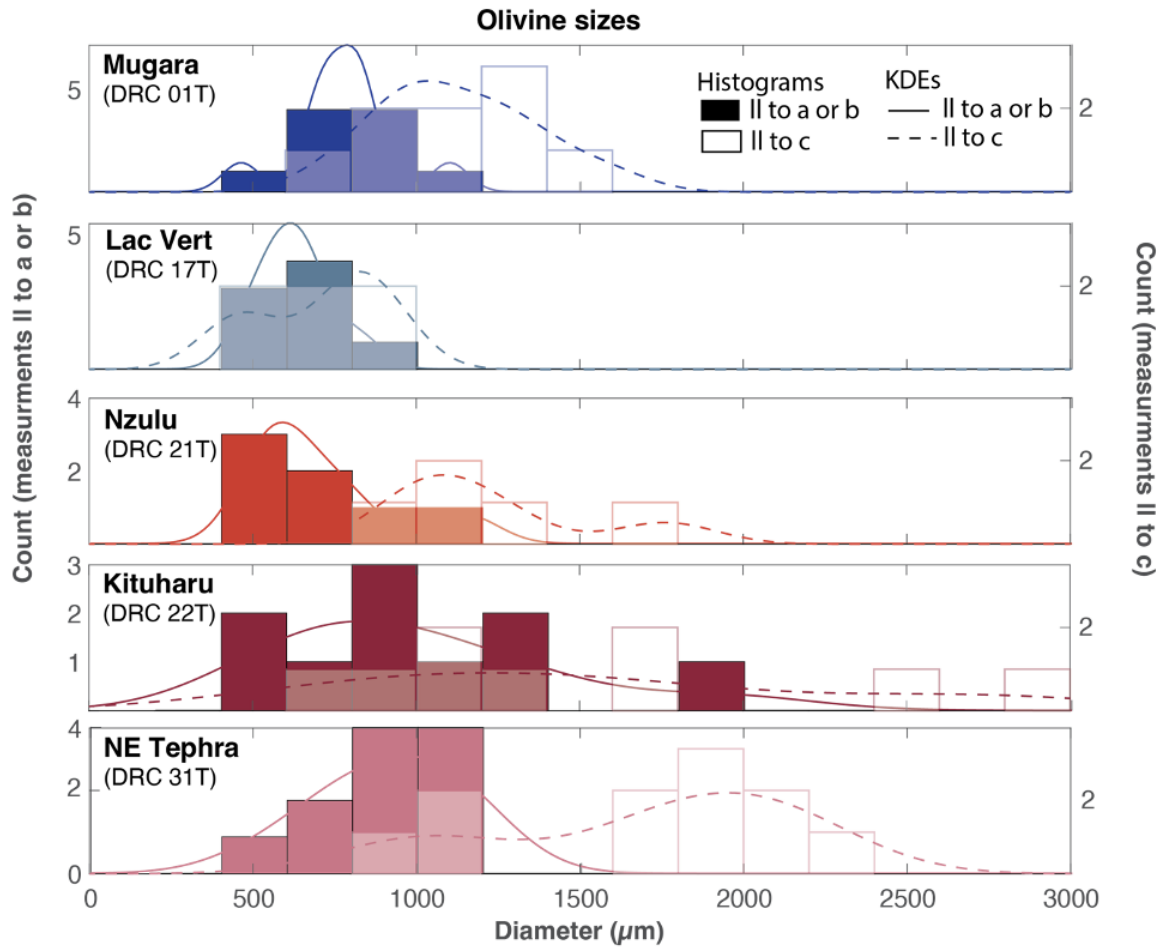


Figure S3. Olivine diameters measured on BSE Images via ImageJ. NE Tephra olivine are the largest (avg = 0.8 mm parallel to a or b, 1.7 mm parallel to c-axis), followed by Kituharu (avg = 1.1 mm parallel to a or b axes, 1.5 parallel to c axis), then Nzulu (average = 0.7 parallel to a or b axes, 1.2 parallel to c-axis), then Mugara (average = 0.8 mm parallel to a or b-axes, 1.1 mm parallel to c-axis), and lastly Lac Vert (avg = 0.6 mm parallel to a or b axes, 0.7 parallel to c axes)

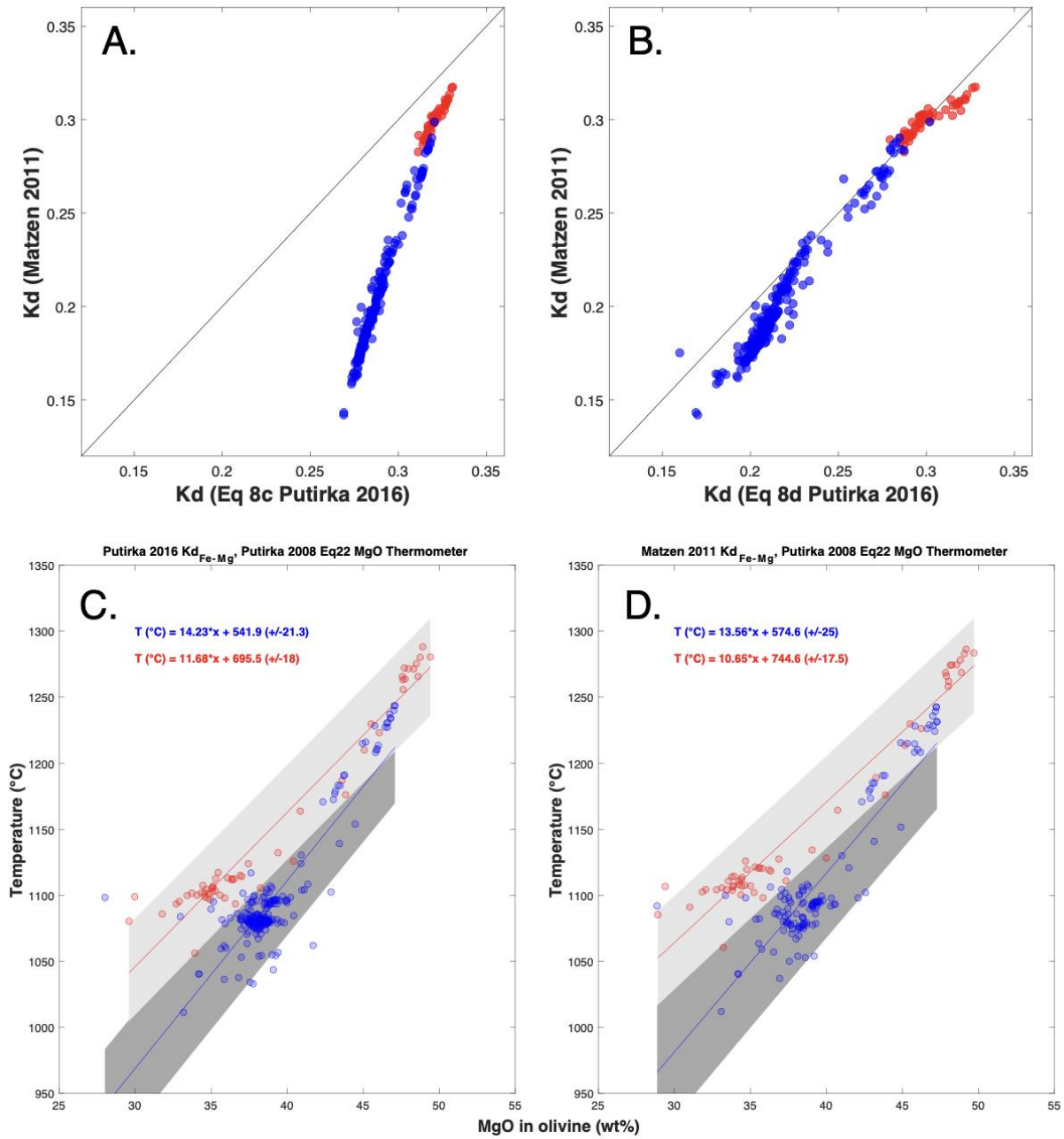


Figure S4. Olivine thermometry equations used to estimate model run temperatures, with data points in red representing compositions from Nyamulagira, and data points in blue representing compositions from Nyiragongo. **A.** Comparisons of K_d values calculated from Equation A2 from Matzen et al. (2011) and K_d values calculated from Equation 8c in Putirka (2016). **B.** Comparisons of K_d values calculated from Equation A2 from Matzen et al. (2011) and K_d values calculated from Equation 8d in Putirka (2016). **C.** Putirka (2016) calculated MgO contents in olivine in equilibrium with whole rock database compositions, against calculated temperatures with the Putirka (2008) olivine thermometer. **D.** Matzen (2011) calculated MgO contents in olivine in equilibrium with whole rock database compositions, against calculated temperatures with the Putirka (2008) olivine thermometer.

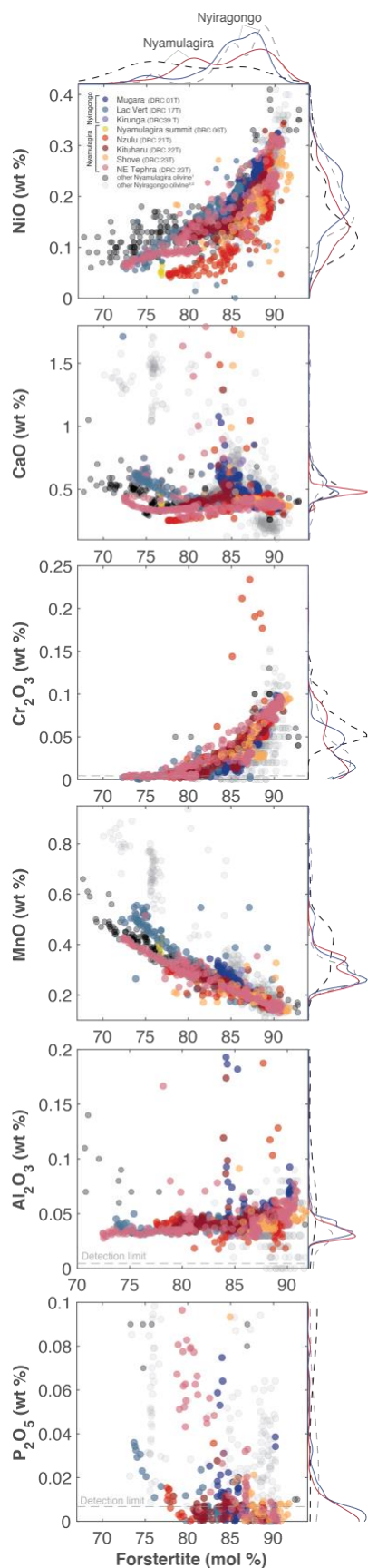


Figure S5. Complete trace elemental analyses in olivine, along with comparisons from Nyiragongo (Molendijk et al., 2024; Molendijk et al., 2025) and Nyamulagira (Katme Kahleghetso et al., 2025)

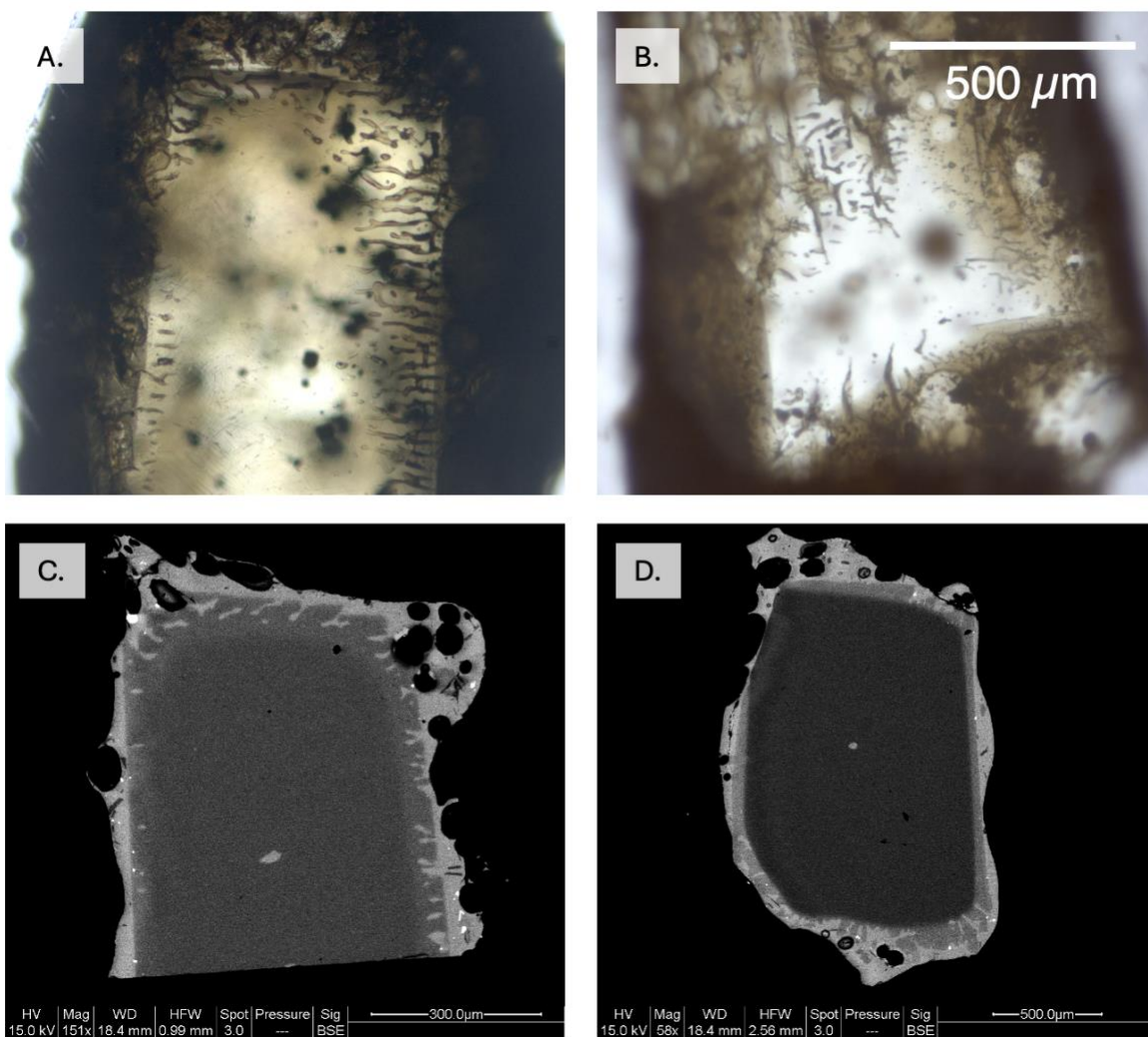


Figure S6 Examples of cellular growth in olivine from DRC31 [NE flank tephra]. A-B. images in transmitted light, C-D images in Backscatter Electron (BSE)

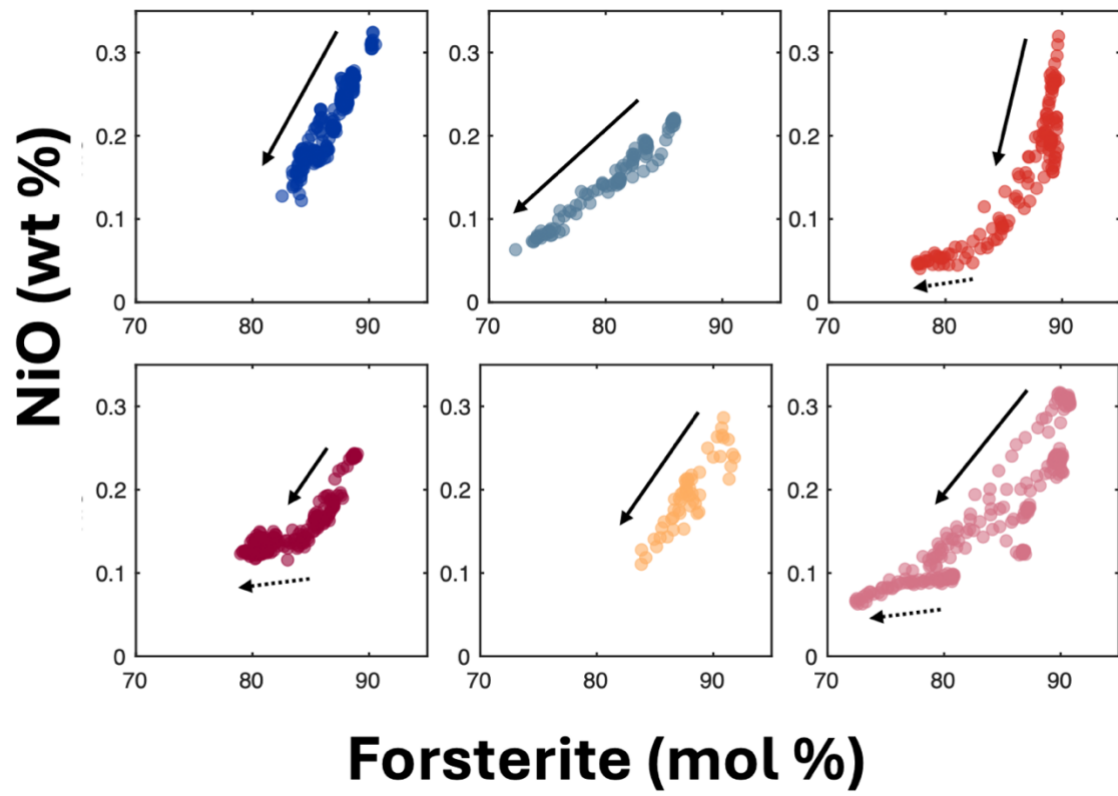


Figure S7. Plots of forsterite versus NiO content in olivine for each tephra unit. Relatively linear trends in NiO versus Fo are the result of mixing, whereas changes in slope indicating differing partitioning behavior of Ni indicate growth processes.

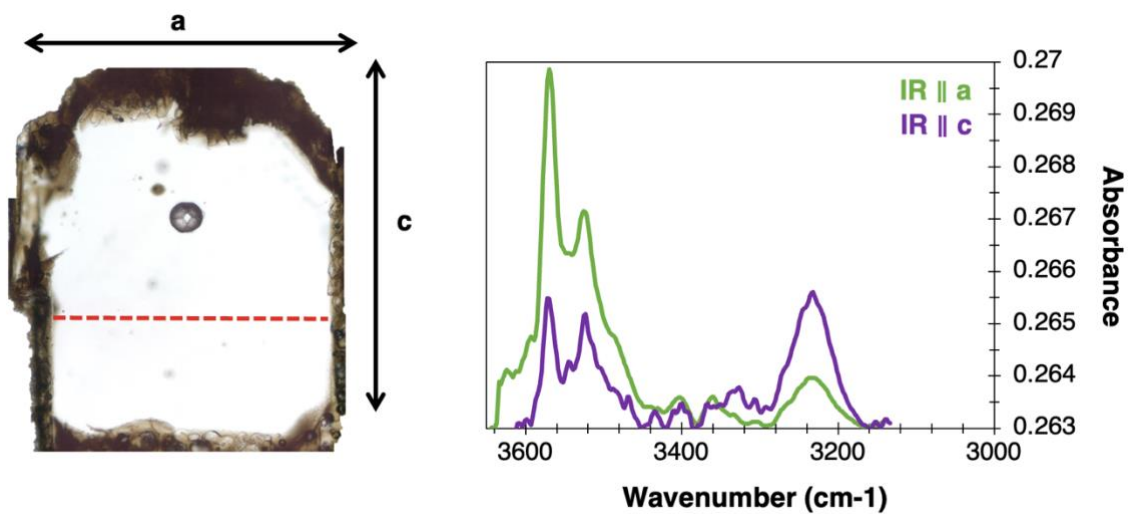


Figure S7. Examples of oriented olivine for FTIR analysis, and IR spectra parallel to the a and c axes

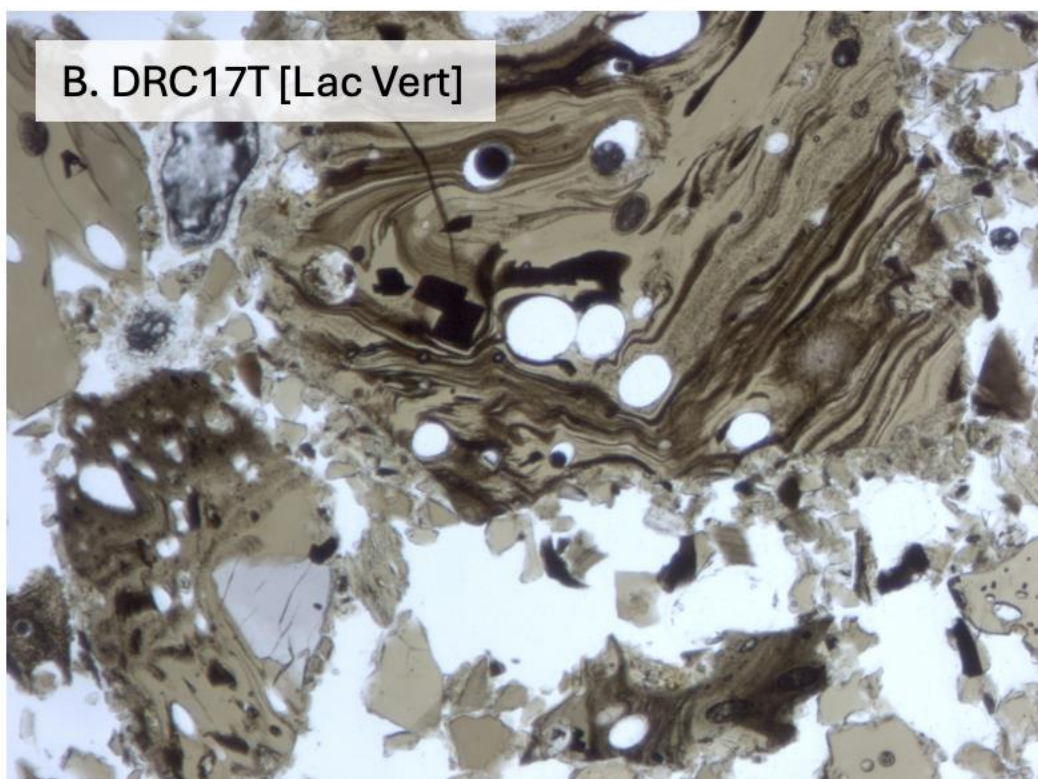
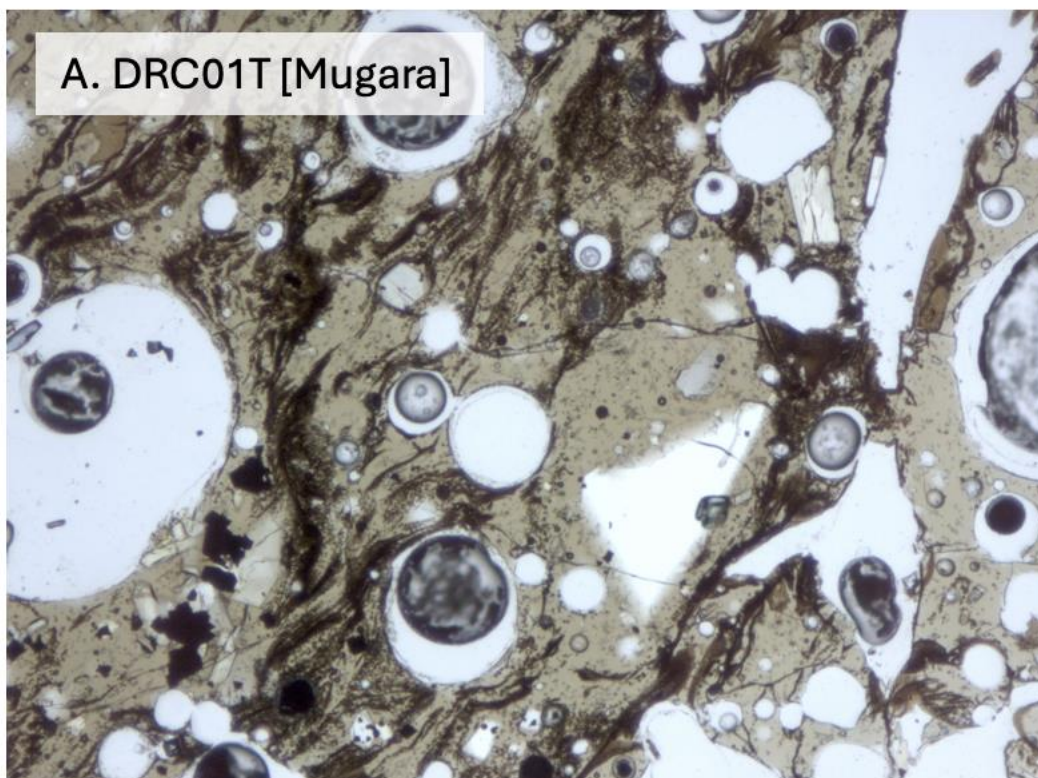


Figure S8. Examples of glass heterogeneity in thin section

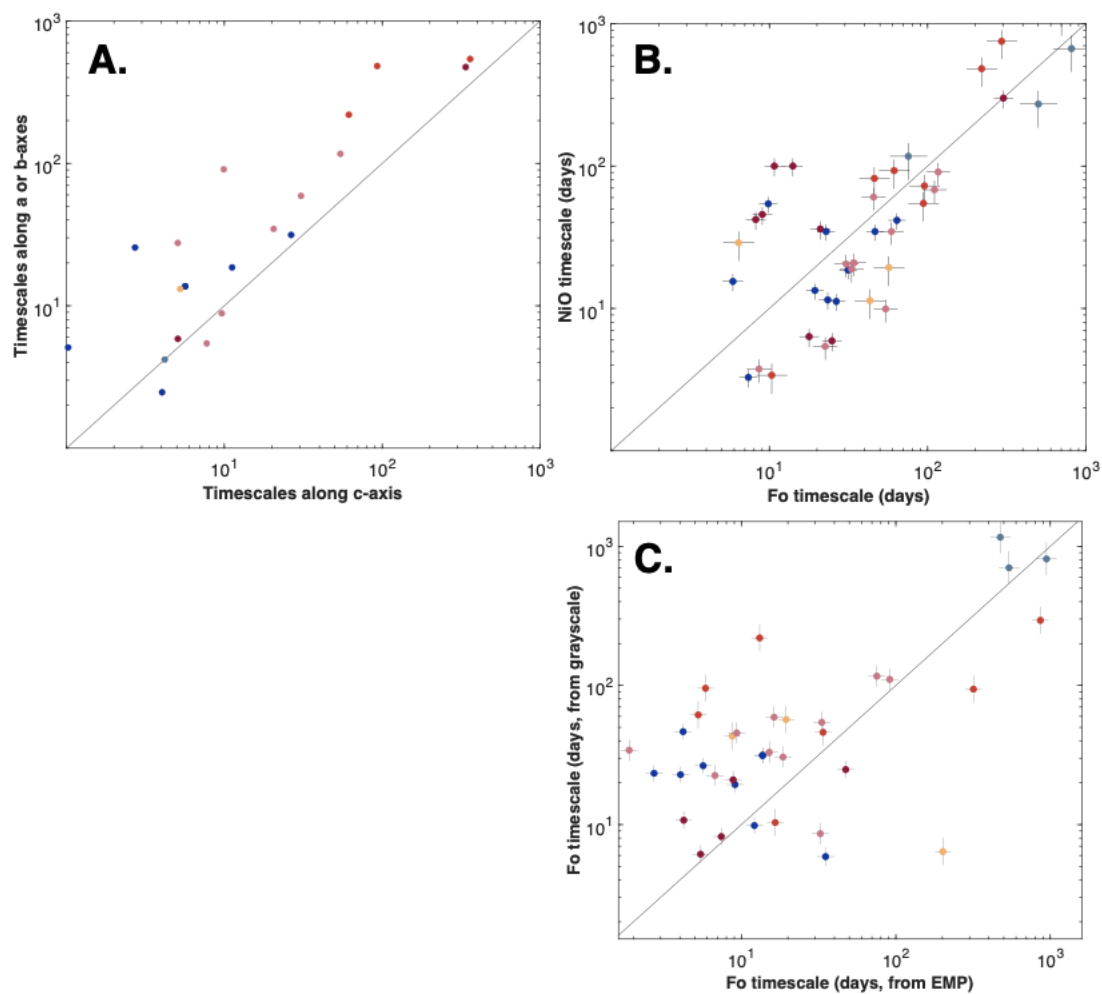


Figure S9. **A.** Comparisons of modeled timescales along the c-axis versus modeled timescales along the a-axis. **B.** Comparisons of modeled timescales for Fo versus modeled timescales for Ni. **C.** Comparisons of modeled timescales for Fo and Fo calculated from grayscale.

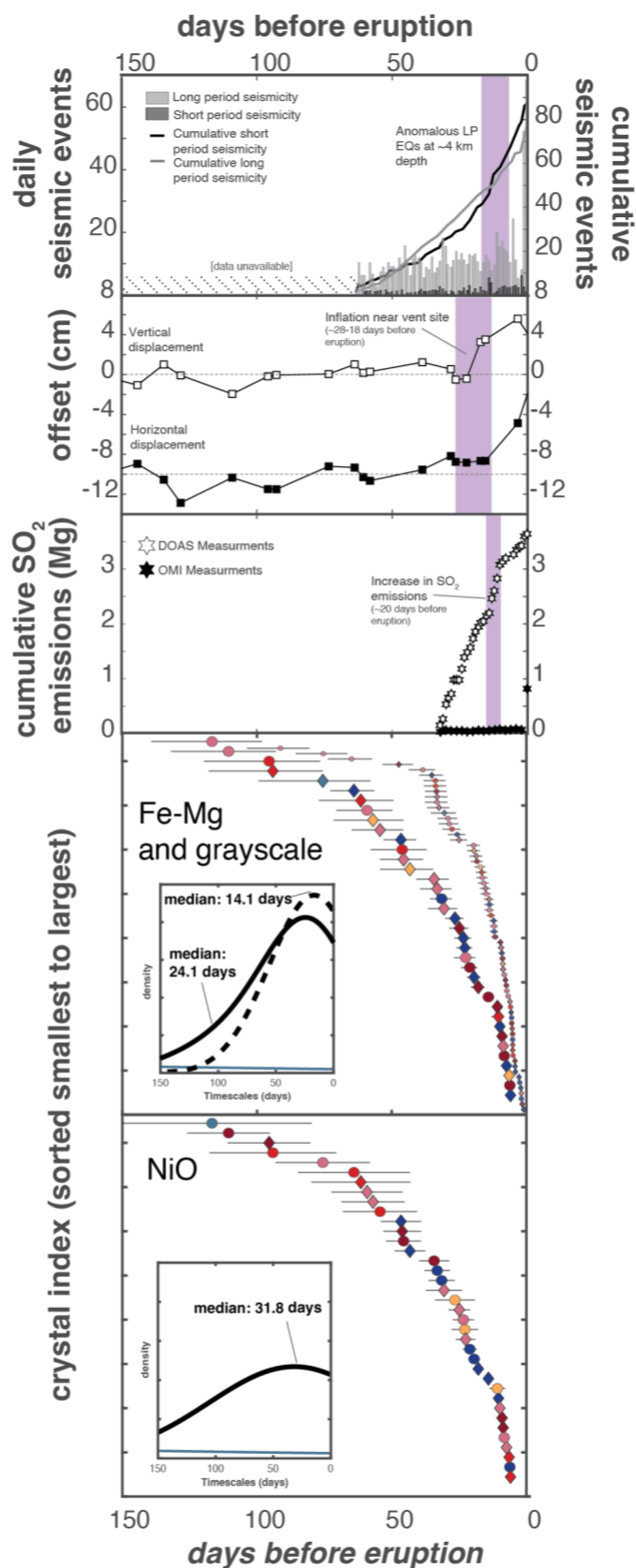


Figure S10. Diffusion timescales below 150 days, and monitoring data preceding the 2010 Nyamulagira flank eruption (Smets et al. 2014). Zones in purple identify time periods of precursory signals. A: Long period and short period seismicity measured at Luboga station. Purple zone indicates the onset of earthquakes at ~4km depth, anomalous in comparison to background seismicity. B: Horizontal and vertical displacement at the 2010 flank vent site, determined using multidimensional small baseline subset method on SAR interferograms. Horizontal displacement is shown offset by -10 cm for clarity. Purple zone highlights inflation near the vent site. C: Estimates of daily SO_2 emissions from a DOAS station and from OMI. Purple zone indicates a period of increasing SO_2 emissions by DOAS. D: Timescales from Fe-Mg and Fe-Mg from grayscale diffusion, showing medians at 24.1 and 14.1 days. E: Timescales from NiO diffusion, showing a median at 31.8 days.

REFERENCES CITED

Chapter II

- Aiuppa, A., Lo Coco, E., Liuzzo, M., Giudice, G., Giuffrida, G., Moretti, R., 2016. Terminal Strombolian activity at Etna's central craters during summer 2012: The most CO₂-rich volcanic gas ever recorded at Mount Etna. *Geochem. J.* 50, 123–138. <https://doi.org/10.2343/geochemj.2.0395>
- Aiuppa, A., Casetta, F., Colorti, M., Stagno, V., Tamburello, G., 2021. Carbon concentration increases with depth of melting in Earth's upper mantle. 2021, Scientific Investigations Report 14, 697–703. <https://doi.org/10.1038/s41561-021-00797-y>
- Aoki, K.-I., Yoshida, T., Yusa, K., Nakamura, Y., 1985. Petrology and geochemistry of the Nyamuragira volcano, Zaire. *Journal of Volcanology and Geothermal Research* 25, 1–28. [https://doi.org/10.1016/0377-0273\(85\)90002-2](https://doi.org/10.1016/0377-0273(85)90002-2)
- Balagizi, C., Mashagiro, N., Kasereka, M., Kelly, P. (2023) Pre- and post-eruptive gas composition measurements at Nyiragongo Volcano, East Africa, using a portable Multi-GAS, EGU 2023, <https://doi.org/10.5194/egusphere-egu23-16823>
- Barette, F., Poppe, S., Smets, B., Benbakkar, M., Kervyn, M., 2017. Spatial variation of volcanic rock geochemistry in the Virunga Volcanic Province: Statistical analysis of an integrated database. *Journal of African Earth Sciences* 134, 888–903. <https://doi.org/10.1016/j.jafrearsci.2016.09.018>
- Barrière, J., d'Oreye, N., Smets, B., Oth, A., Delhay, L., Subira, J., Mashagiro, N., Derauw, D., Smittarello, D., Syavulisembo, A.M., Kervyn, F., 2022. Intra-Crater Eruption Dynamics at Nyiragongo (D.R. Congo), 2002–2021. *Journal of Geophysical Research: Solid Earth* 127(4), e2021JB023858. <https://doi.org/10.1029/2021JB023858>
- Bobrowski, N., Giuffrida, G.B., Yalire, M., Lübcke, P., Arellano, S., Balagizi, C., Calabrese, S., Galle, B., Tedesco, D., 2017a. Multi-component gas emission measurements of the active lava lake of Nyiragongo, DR Congo. *Journal of*

- African Earth Sciences 134, 856–865.
<https://doi.org/10.1016/j.jafrearsci.2016.07.010>
- Bobrowski, N., Giuffrida, G.B., Arellano, S., Yalire, M., Liotta, M., Brusca, L., Calabrese, S., Scaglione, S., Rüdiger, J., Castro, J.M., Galle, B., Tedesco, D., 2017b. Plume composition and volatile flux of Nyamulagira volcano, Democratic Republic of Congo, during birth and evolution of the lava lake, 2014–2015. *Bull Volcanol* 79, 90. <https://doi.org/10.1007/s00445-017-1174-0>
- Boudoire, G, N Bobrowski, P-Y Burgi, S Calabrese, L France, G Giuffrida, F Grassa, et al. “Magmatic Activity in Incipient Continental Break-Up as Revealed by Coupling Melt and Fluid Inclusions.” *Journal of Petrology* 65, no. 12 (December 1, 2024): egae125. <https://doi.org/10.1093/petrology/egae125>.
- Boudoire, G., Giuffrida, G., Liuzzo, M., Bobrowski, N., Calabrese, S., Kuhn, J., Mwepu, J.-C.K., Grassa, F., Caliro, S., Rizzo, A.L., Italiano, F., Yalire, M., Karume, K., Syavulisembo, A.M., Tedesco, D., 2022. Chemical variability in volcanic gas plumes and fumaroles along the East African Rift System: New insights from the Western Branch. *Chemical Geology* 596, 120811.
<https://doi.org/10.1016/j.chemgeo.2022.120811>
- Brounce, Maryjo, Sara Scoggins, Tobias P. Fischer, Heather Ford, and Joseph Byrnes. “Volatiles and Redox Along the East African Rift.” *Geochemistry, Geophysics, Geosystems* 25, no. 8 (August 2024): e2024GC011657.
<https://doi.org/10.1029/2024GC011657>.
- 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, 273–289. <https://doi.org/10.1016/j.chemgeo.2008.11.010>
- Demant, A., Lestrade, P., Lubala, R.T., Kampunzu, A.B., Durieux, J., 1994. Volcanological and petrological evolution of Nyiragongo volcano, Virunga volcanic field, Zaire. *Bull Volcanol* 56, 47–61.
<https://doi.org/10.1007/BF00279728>
- De Moor, J.M., Fischer, T.P., Sharp, Z.D., King, P.L., Wilke, M., Botcharnikov, R.E., Cottrell, E., Zelenski, M., Marty, B., Klimm, K., Rivard, C., Ayalew, D.,

- Ramirez, C., Kelley, K.A., 2013. Sulfur degassing at Erta Ale (Ethiopia) and Masaya (Nicaragua) volcanoes: Implications for degassing processes and oxygen fugacities of basaltic systems. *Geochem Geophys Geosyst* 14, 4076–4108.
<https://doi.org/10.1002/ggge.20255>
- DeVitre, C.L., Gazel, E., Ramalho, R.S., Venugopal, S., Steele-MacInnis, M., Hua, J., Allison, C.M., Moore, L.R., Carracedo, J.C., Monteleone, B., 2023. Oceanic intraplate explosive eruptions fed directly from the mantle. *Proceedings of the National Academy of Sciences* 120, e2302093120.
<https://doi.org/10.1073/pnas.2302093120>
- Ding, S., Plank, T., Wallace, P.J., Rasmussen, D.J., 2023. Sulfur_X: A Model of Sulfur Degassing During Magma Ascent. *Geochem Geophys Geosyst* 24, e2022GC010552. <https://doi.org/10.1029/2022GC010552>
- Fischer, T.P., Arellano, S., Carn, S., Aiuppa, A., Galle, B., Allard, P., Lopez, T., Shinohara, H., Kelly, P., Werner, C., Cardellini, C., Chiodini, G., 2019. The emissions of CO₂ and other volatiles from the world's subaerial volcanoes. *Sci Rep* 9, 18716. <https://doi.org/10.1038/s41598-019-54682-1>
- Flemetakis, S., Klemme, S., Stracke, A., Genske, F., Berndt, J., Rohrbach, A., 2021. Constraining the presence of amphibole and mica in metasomatized mantle sources through halogen partitioning experiments. *Lithos* 380–381, 105859.
<https://doi.org/10.1016/j.lithos.2020.105859>
- Foley, S.F., Ezad, I.S., Van Der Laan, S.R., Pertermann, M., 2022. Melting of hydrous pyroxenites with alkali amphiboles in the continental mantle: 1. Melting relations and major element compositions of melts. *Geoscience Frontiers* 13, 101380.
<https://doi.org/10.1016/j.gsf.2022.101380>
- Foley, S.F., Fischer, T.P., 2017. An essential role for continental rifts and lithosphere in the deep carbon cycle. *Nature Geosci* 10, 897–902.
<https://doi.org/10.1038/s41561-017-0002-7>
- Foley, S.F., Musselwhite, D.S., Van Der Laan, S.R., 1999. Melt Compositions from Ultramafic Vein Assemblages in the Lithospheric Mantle: a Comparison of Cratonic and Non-Cratonic Settings, in: *Proceedings of the VIIth International Kimberlite Conference: University of Cape Town, South Africa. Presented at the*

- Meeting Name: International Kimberlite Conference, Red Roof Design cc, Cape Town.
- Foley, S., 1992. Vein-plus-wall-rock melting mechanisms in the lithosphere and the origin of potassic alkaline magmas. *Lithos* 28, 435–453.
[https://doi.org/10.1016/0024-4937\(92\)90018-T](https://doi.org/10.1016/0024-4937(92)90018-T)
- Ghiorso, M.S., Gualda, G.A.R., 2015. An H₂O–CO₂ mixed fluid saturation model compatible with rhyolite-MELTS. *Contrib Mineral Petrol* 169, 53.
<https://doi.org/10.1007/s00410-015-1141-8>
- Gualda, G.A.R., Ghiorso, M.S., Lemons, R.V., Carley, T.L., 2012. Rhyolite-MELTS: a Modified Calibration of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems. *Journal of Petrology* 53, 875–890.
<https://doi.org/10.1093/petrology/egr080>
- Head, E.M., Shaw, A.M., Wallace, P.J., Sims, K.W.W., Carn, S.A., 2011. Insight into volatile behavior at Nyamuragira volcano (D.R. Congo, Africa) through olivine-hosted melt inclusions: Volatile Behavior at Nyamuragira Volcano. *Geochem. Geophys. Geosyst.* 12, n/a-n/a. <https://doi.org/10.1029/2011GC003699>
- Hecker, J.G., Marks, M.A.W., Wenzel, T., Markl, G., 2020. Halogens in amphibole and mica from mantle xenoliths: Implications for the halogen distribution and halogen budget of the metasomatized continental lithosphere. *American Mineralogist* 105, 781–794. <https://doi.org/10.2138/am-2020-7174>
- Hudgins, T.R., Mukasa, S.B., Simon, A.C., Moore, G., Barifaijo, E., 2015. Melt inclusion evidence for CO₂-rich melts beneath the western branch of the East African Rift: implications for long-term storage of volatiles in the deep lithospheric mantle. *Contrib Mineral Petrol* 169, 46. <https://doi.org/10.1007/s00410-015-1140-9>
- Hunt, J.A., Zafu, A., Mather, T.A., Pyle, D.M., Barry, P.H., 2017. Spatially Variable CO₂ Degassing in the Main Ethiopian Rift: Implications for Magma Storage, Volatile Transport, and Rift-Related Emissions. *Geochem Geophys Geosyst* 18, 3714–3737. <https://doi.org/10.1002/2017GC006975>
- Iddon, F., Edmonds, M., 2020. Volatile-Rich Magmas Distributed Through the Upper Crust in the Main Ethiopian Rift. *Geochemistry, Geophysics, Geosystems* 21(6), e2019GC008904. <https://doi.org/10.1029/2019GC008904>

- Innocenzi, F., Ronca, S., Foley, S., Agostini, S., Lustrino, M., 2024. Carbonatite and ultrabasic magmatism at Toro Ankole and Virunga, western branch of the East African Rift system. *Gondwana Research* 125, 317–342.
<https://doi.org/10.1016/j.gr.2023.09.005>
- Kamate Kaleghetso, E., Namur, O., Smets, B., Vander Auwera, J., Lubala, F., Van Gerve, T., Molendijk, S.M., 2024. Magmatic differentiation and plumbing system beneath Nyamulagira volcano (Virunga Volcanic Province, East African Rift). *Journal of Volcanology and Geothermal Research* 458, 108264.
<https://doi.org/10.1016/j.jvolgeores.2024.108264>
- Lamb, W.M., Popp, R.K., 2009. Amphibole equilibria in mantle rocks: Determining values of mantle $a_{\text{H}_2\text{O}}$ and implications for mantle H_2O contents. *American Mineralogist* 94, 41–52. <https://doi.org/10.2138/am.2009.2950>
- Lee, H., Muirhead, J.D., Fischer, T.P., Ebinger, C.J., Kattenhorn, S.A., Sharp, Z.D., Kianji, G., 2016. Massive and prolonged deep carbon emissions associated with continental rifting. *Nature Geosci* 9, 145–149. <https://doi.org/10.1038/ngeo2622>
- Le Guern, F., 1987. Mechanism of energy transfer in the lava lake of Niragongo (Zaire), 1959–1977. *Journal of Volcanology and Geothermal Research* 31, 17–31.
[https://doi.org/10.1016/0377-0273\(87\)90003-5](https://doi.org/10.1016/0377-0273(87)90003-5)
- Lerner, A.H., Muth, M.J., Wallace, P.J., Lanzirotti, A., Newville, M., Gaetani, G.A., Chowdhury, P., Dasgupta, R., 2021. Improving the reliability of Fe- and S-XANES measurements in silicate glasses: Correcting beam damage and identifying Fe-oxide nanolites in hydrous and anhydrous melt inclusions. *Chemical Geology* 586, 120610. <https://doi.org/10.1016/j.chemgeo.2021.120610>
- Lloyd, F.E., Arima, M., Edgar, A.D., 1985. Partial melting of a phlogopite-clinopyroxenite nodule from south-west Uganda: an experimental study bearing on the origin of highly potassic continental rift volcanics. *Contr. Mineral. and Petrol.* 91, 321–329. <https://doi.org/10.1007/BF00374688>
- Louaradi, D., 1994. Etudes isotopique (C, O) et microthermométrie des magmas alcalins et carbonatiques du Rift Est Africain et de la presqu'île Kola (PhD Thesis). Institut de physique du globe de Paris: Géochimie des Isotopes Stables.

- Mavonga, T., Zana, N., Durrheim, R.J., 2010. Studies of crustal structure, seismic precursors to volcanic eruptions and earthquake hazard in the eastern provinces of the Democratic Republic of Congo. *Journal of African Earth Sciences* 58, 623–633. <https://doi.org/10.1016/j.jafrearsci.2010.08.008>
- Médard, E., Schmidt, M.W., Schiano, P., Ottolini, L., 2006. Melting of Amphibole-bearing Wehrlites: an Experimental Study on the Origin of Ultra-calcic Nepheline-normative Melts. *Journal of Petrology* 47, 481–504. <https://doi.org/10.1093/petrology/egi083>
- Michael, P.J., Graham, D.W., 2015. The behavior and concentration of CO₂ in the suboceanic mantle: Inferences from undegassed ocean ridge and ocean island basalts. *Lithos* 236–237, 338–351. <https://doi.org/10.1016/j.lithos.2015.08.020>
- Minissale, S., Casalini, M., Cucciniello, C., Balagizi, C., Tedesco, D., Boudoire, G., Morra, V., Melluso, L., 2022. The geochemistry of recent Nyamulagira and Nyiragongo potassic lavas, Virunga Volcanic Province, and implications on the enrichment processes in the mantle lithosphere of the Tanzania-Congo craton. *Lithos* 420–421, 106696. <https://doi.org/10.1016/j.lithos.2022.106696>
- Minissale, S., Zanetti, A., Tedesco, D., Morra, V., Melluso, L., 2019. The petrology and geochemistry of Nyiragongo lavas of 2002, 2016, 1977 and 2017 AD, and the trace element partitioning between melilitite glass and melilite, nepheline, leucite, clinopyroxene, apatite, olivine and Fe-Ti oxides: a unique scenario. *Lithos* 332–333, 296–311. <https://doi.org/10.1016/j.lithos.2019.02.023>
- Molendijk, S., Namur, O., Neave, D.A. 2025, Mantle Sources Underlying Nyiragongo Volcano.” *Chemical Geology* 675: 122607. <https://doi.org/10.1016/j.chemgeo.2024.122607>.
- Molendijk, S.M., Namur, O., Kamate Kaleghetso, E., Mason, P.R.D., Smets, B., Vander Auwera, J., Neave, D.A., 2024. Plumbing System Architecture and Differentiation Processes of the Nyiragongo Volcano, DR Congo. *Journal of Petrology* 65, egad088. <https://doi.org/10.1093/petrology/egad088>
- Molendijk, S.M., Namur, O., Mason, P.R.D., Dubacq, B., Smets, B., Neave, D.A., Charlier, B., 2023. Trace element partitioning in silica-undersaturated alkaline

- magmatic systems. *Geochimica et Cosmochimica Acta* 346, 29–53.
<https://doi.org/10.1016/j.gca.2023.01.025>
- Muth, M.J., Cottrell, E., 2023. No Detectable Redox Exchange between Sulfur and Iron during Rapid Cooling of Basalts.” *Earth and Planetary Science Letters* 616: 118210. <https://doi.org/10.1016/j.epsl.2023.118210>.
- Oppenheimer, C., Kyle, P.R., 2008. Probing the magma plumbing of Erebus volcano, Antarctica, by open-path FTIR spectroscopy of gas emissions. *Journal of Volcanology and Geothermal Research* 177, 743–754.
<https://doi.org/10.1016/j.jvolgeores.2007.08.022>
- Phillips, E.H., 2015. Mantle Sources, Eruptive Cyclicity, and Magmatic Evolution at Nyiragongo and Nyamulagira Volcanoes, Virunga Volcanic Province, DR Congo. Doctoral Thesis, University of Wyoming
- Pilet, S., Baker, M.B., Stolper, E.M., 2008. Metasomatized Lithosphere and the Origin of Alkaline Lavas. *Science* 320, 916–919. <https://doi.org/10.1126/science.1156563>
- Platz, T., Foley, S.F., André, L., 2004. Low-pressure fractionation of the Nyiragongo volcanic rocks, Virunga Province, D.R. Congo. *Journal of Volcanology and Geothermal Research* 136, 269–295.
<https://doi.org/10.1016/j.jvolgeores.2004.05.020>
- Poppe, S., Smets, B., Fontijn, K., Rukeza, M.B., De Marie Fikiri Migabo, A., Milungu, A.K., Namogo, D.B., Kervyn, F., Kervyn, M., 2016. Holocene phreatomagmatic eruptions alongside the densely populated northern shoreline of Lake Kivu, East African Rift: timing and hazard implications. *Bull Volcanol* 78, 82.
<https://doi.org/10.1007/s00445-016-1074-8>
- Pouclet A , Bram K (2021) Nyiragongo and Nyamuragira: a review of volcanic activity in the Kivu rift, western branch of the East African Rift System. *Bull Volcanol* 83 :10
- Pouclet, A., 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: 219–46. <https://doi.org/10.1016/j.jafrearsci.2016.05.026>.

- Prelević, D., Förster, M.W., Buhre, S., Gülmez, F., Grützner, T., Wang, Y., Foley, S.F. (2024) Recent Advances Made by Reaction Experiments on Melting of Heavily Metasomatized Hydrous Mantle. *Earth-Science Reviews* 256 : 104881. <https://doi.org/10.1016/j.earscirev.2024.104881>.
- Rasmussen, D.J., Plank, T.A., Wallace, P.J., Newcombe, M.E., Lowenstern, J.B., 2020. Vapor-bubble growth in olivine-hosted melt inclusions. *American Mineralogist* 105, 1898–1919. <https://doi.org/10.2138/am-2020-7377>
- Righter, K., Dyar, M.D., Delaney, J.S., Vennemann, T.W., Hervig, R.L., King, P.L., 2002. Correlations of octahedral cations with OH⁻, O₂⁻, Cl⁻, and F⁻ in biotite from volcanic rocks and xenoliths. *American Mineralogist* 87, 142–153. <https://doi.org/10.2138/am-2002-0115>
- Rooney, T.O., Wallace, P.J., Muirhead, J.D., Chiasera, B., Steiner, R.A., Girard, G., Karson, J.A., 2022. Transition to magma-driven rifting in the South Turkana Basin, Kenya: Part 2. *JGS* 179, jgs2021-160. <https://doi.org/10.1144/jgs2021-160>
- 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, 236–248. <https://doi.org/10.1016/j.epsl.2009.04.036>
- Ross, K.A., Smets, B., De Batist, M., Hilbe, M., Schmid, M., Anselmetti, F.S., 2014. Lake-level rise in the late Pleistocene and active subaquatic volcanism since the Holocene in Lake Kivu, East African Rift. *Geomorphology* 221, 274–285. <https://doi.org/10.1016/j.geomorph.2014.05.010>
- 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: Magma degassing at Nyiragongo Volcano. *Geochem. Geophys. Geosyst.* 9, n/a-n/a. <https://doi.org/10.1029/2007GC001829>
- 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, 837–846. <https://doi.org/10.1016/j.jvolgeores.2008.09.017>
- Smets, B., Kervyn, M., d'Oreye, N., Kervyn, F., 2015. Spatio-temporal dynamics of eruptions in a youthful extensional setting: Insights from Nyamulagira Volcano

- (D.R. Congo), in the western branch of the East African Rift. *Earth-Science Reviews* 150, 305–328. <https://doi.org/10.1016/j.earscirev.2015.08.008>
- Smittarello, D., Smets, B., Barrière, J., Michellier, C., Oth, A., Shreve, T., Grandin, R., Theys, N., Brenot, H., Cayol, V., Allard, P., Caudron, C., Chevrel, O., Darchambeau, F., De Buyl, P., Delhay, L., Derauw, D., Ganci, G., Geirsson, H., Kamate Kaleghetso, E., Kambale Makundi, J., Kambale Nguomoja, I., Kasereka Mahinda, C., Kervyn, M., Kimanuka Ruriho, C., Le Mével, H., Molendijk, S., Namur, O., Poppe, S., Schmid, M., Subira, J., Wauthier, C., Yalire, M., d'Oreye, N., Kervyn, F., Syavulisembo Muhindo, A., 2022. Precursor-free eruption triggered by edifice rupture at Nyiragongo volcano. *Nature* 609, 83–88. <https://doi.org/10.1038/s41586-022-05047-8>
- Sublett, D.M., 2019. PVTX and Raman Spectral Properties of Fluids at Elevated Pressures and Temperatures (PhD Thesis). Virginia Polytechnic Institute and State University.
- Sun, C., Dasgupta, R., 2023. Carbon budget of Earth's deep mantle constrained by petrogenesis of silica-poor ocean island basalts. *Earth and Planetary Science Letters* 611, 118135. <https://doi.org/10.1016/j.epsl.2023.118135>
- Sun, C., Dasgupta, R., 2020. Thermobarometry of CO₂-rich, silica-undersaturated melts constrains cratonic lithosphere thinning through time in areas of kimberlitic magmatism. *Earth and Planetary Science Letters* 550, 116549. <https://doi.org/10.1016/j.epsl.2020.116549>
- Wauthier, C., Cayol, V., Smets, B., d'Oreye, N., Kervyn, F., 2015. Magma Pathways and Their Interactions Inferred from InSAR and Stress Modeling at Nyamulagira Volcano, D.R. Congo. *Remote Sensing* 7, 15179–15202. <https://doi.org/10.3390/rs71115179>
- Wauthier, C., Cayol, V., Kervyn, F., d'Oreye, N., 2012. Magma sources involved in the 2002 Nyiragongo eruption, as inferred from an InSAR analysis. *Journal of Geophysical Research: Solid Earth* 117. <https://doi.org/10.1029/2011JB008257>
- Wieser, P., Gleeson, M., 2023. PySulfSat: An open-source Python3 tool for modeling sulfide and sulfate saturation. *Volcanica* 6, 107–127. <https://doi.org/10.30909/vol.06.01.107127>

- Wieser, P.E., Iacovino, K., Matthews, S., Moore, G., Allison, C.M., 2022. VESIcal: 2. A Critical Approach to Volatile Solubility Modeling Using an Open-Source Python3 Engine. *Earth and Space Science* 9, e2021EA001932.
<https://doi.org/10.1029/2021EA001932>
- Wong, K., Ferguson, D., Wieser, P., Morgan, D., Edmonds, M., Tadesse, A.Z., Yirgu, G., Harvey, J., Hammond, S., 2023. Focused Mid-Crustal Magma Intrusion During Continental Break-Up in Ethiopia. *Geophysical Research Letters* 50(11), e2023GL103257. <https://doi.org/10.1029/2023GL103257>

Chapter III

- Allison, C.M., Roggensack, K., Clarke, A.B., 2022. MafCH: a general model for H₂O–CO₂ solubility in mafic magmas. *Contrib Mineral Petrol* 177, 40.
<https://doi.org/10.1007/s00410-022-01903-y>
- Aoki, K., Kurasawa, H., 1984. Sr isotope study of the tephrite series from Nyamuragira volcano, Zaire. *Geochem. J.* 18, 95–100. <https://doi.org/10.2343/geochemj.18.95>
- Arevalo Jr, R., & McDonough, W. F. (2010). Chemical variations and regional diversity observed in MORB. *Chemical Geology*, 271(1-2), 70-85.
- Baasner, A., Médard, E., Laporte, D., & Hoffer, G. (2016). Partial melting of garnet lherzolite with water and carbon dioxide at 3 GPa using a new melt extraction technique: implications for intraplate magmatism. *Contributions to Mineralogy and Petrology*, 171, 1-23.
- Bucholz, C.E., Gaetani, G.A., Behn, M.D., Shimizu, N., 2013. Post-entrapment modification of volatiles and oxygen fugacity in olivine-hosted melt inclusions. *Earth and Planetary Science Letters* 374, 145–155.
<https://doi.org/10.1016/j.epsl.2013.05.033>
- Caron, J.P.H., Kampunzu, A.B., Lubala, R.T., Miruho, K.B., Musengie, M.K., Velluntini, P.J., Brousse, R., n.d. A propos de l'éruption adventive du Nyamulagira de janvier - février 1980: Nature de la lave du nouveau Gasenyi. 1982, *Annales de la Société Géologique de Belgique* 31–40.

- 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, 273–289. <https://doi.org/10.1016/j.chemgeo.2008.11.010>
- Chen, Y., Provost, A., Schiano, P., & Cluzel, N. (2011). The rate of water loss from olivine-hosted melt inclusions. *Contributions to Mineralogy and Petrology*, 162, 625–636. <https://doi.org/10.1007/s00410-012-0821-x>
- Condomines, M., Carpentier, M., & Ongendangenda, T. (2015). Extreme radium deficit in the 1957 AD Mugogo lava (Virunga volcanic field, Africa): Its bearing on olivine-melilitite genesis. *Contributions to Mineralogy and Petrology*, 169, 1–19.
- Cottrell, E., Kelley, K.A., Lanzirotti, A., Fischer, R.A., 2009. High-precision determination of iron oxidation state in silicate glasses using XANES. *Chemical Geology* 268, 167–179. <https://doi.org/10.1016/j.chemgeo.2009.08.008>
- Daly, E., Keir, D., Ebinger, C.J., Stuart, G.W., Bastow, I.D., Ayele, A., 2008. Crustal tomographic imaging of a transitional continental rift: the Ethiopian rift. *Geophysical Journal International* 172, 1033–1048. <https://doi.org/10.1111/j.1365-246X.2007.03682.x>
- Danyushevsky, L.V., Plechov, P., 2011. Petrolog3: Integrated software for modeling crystallization processes. *Geochemistry, Geophysics, Geosystems* 12. <https://doi.org/10.1029/2011GC003516>
- DeVitre, C.L., Gazel, E., Ramalho, R.S., Venugopal, S., Steele-MacInnis, M., Hua, J., Allison, C.M., Moore, L.R., Carracedo, J.C., Monteleone, B., 2023. Oceanic intraplate explosive eruptions fed directly from the mantle. *Proceedings of the National Academy of Sciences* 120, e2302093120. <https://doi.org/10.1073/pnas.23020931204>
- Di Carlo, I. D. A., Pichavant, M., Rotolo, S. G., & Scaillet, B. (2006). Experimental crystallization of a high-K arc basalt: the golden pumice, Stromboli volcano (Italy). *Journal of Petrology*, 47(7), 1317–1343. <https://doi.org/10.1093/petrology/egl011>
- Dixon, J.E., Stolper, E.M., 1995. An Experimental Study of Water and Carbon Dioxide Solubilities in Mid-Ocean Ridge Basaltic Liquids. Part II: Applications to

- Degassing. *Journal of Petrology*.
<https://doi.org/10.1093/oxfordjournals.petrology.a037268>
- Dixon, J.E., 1997. Degassing of alkalic basalts. *American Mineralogist* 82, 368–378.
<https://doi.org/10.2138/am-1997-3-415>
- Dupuy, C., Liotard, J.M., Dostal, J., 1992. Zr/hf fractionation in intraplate basaltic rocks: Carbonate metasomatism in the mantle source. *Geochimica et Cosmochimica Acta* 56, 2417–2423. [https://doi.org/10.1016/0016-7037\(92\)90198-R](https://doi.org/10.1016/0016-7037(92)90198-R)
- Fedorov A., Beichel R., Kalpathy-Cramer J., Finet J., Fillion-Robin J-C., Pujol S., Bauer C., Jennings D., Fennessy F., Sonka M., Buatti J., Aylward S.R., Miller J.V., Pieper S., Kikinis R. 3D Slicer as an Image Computing Platform for the Quantitative Imaging Network. *Magnetic Resonance Imaging*. 2012 Nov;30(9):1323-41. PMID: 22770690.
- Furman, T., Graham, D., 1999. Erosion of lithospheric mantle beneath the East African Rift system: geochemical evidence from the Kivu volcanic province.
- Gaetani, G.A., O’Leary, J.A., Shimizu, N., Bucholz, C.E., Newville, M., 2012. Rapid reequilibration of H₂O and oxygen fugacity in olivine-hosted melt inclusions. *Geology* 40, 915–918. <https://doi.org/10.1130/G32992.1>
- Gualda, G.A.R., Ghiorso, M.S., Lemons, R.V., Carley, T.L., 2012. Rhyolite-MELTS: a Modified Calibration of MELTS Optimized for Silica-rich, Fluid-bearing Magmatic Systems. *Journal of Petrology* 53, 875–890. <https://doi.org/10.1093/petrology/egr080>
- Hanyu, T., Yamamoto, J., Kimoto, K., Shimizu, K., Ushikubo, T., 2020. Determination of total CO₂ in melt inclusions with shrinkage bubbles. *Chemical Geology* 557, 119855. <https://doi.org/10.1016/j.chemgeo.2020.119855>
- Iacovino, K., Oppenheimer, C., Scaillet, B., Kyle, P., 2016. Storage and Evolution of Mafic and Intermediate Alkaline Magmas beneath Ross Island, Antarctica. *J. Petrology* 57, 93–118. <https://doi.org/10.1093/petrology/egv083>
- Jochum, K.P., Seufert, H.M., Spettel, B., Palme, H., 1986. The solar-system abundances of Nb, Ta, and Y, and the relative abundances of refractory lithophile elements in differentiated planetary bodies. *Geochimica et Cosmochimica Acta* 50, 1173–1183. [https://doi.org/10.1016/0016-7037\(86\)90400-X](https://doi.org/10.1016/0016-7037(86)90400-X)

- Jugo, P.J., Wilke, M., Botcharnikov, R.E., 2010. Sulfur K-edge XANES analysis of natural and synthetic basaltic glasses: Implications for S speciation and S content as function of oxygen fugacity. *Geochimica et Cosmochimica Acta* 74, 5926–5938. <https://doi.org/10.1016/j.gca.2010.07.022>
- Kamate Kaleghetso, E., Namur, O., Smets, B., Vander Auwera, J., Lubala, F., Van Gerve, T., Molendijk, S.M., 2025. Magmatic differentiation and plumbing system beneath Nyamulagira volcano (Virunga Volcanic Province, East African Rift). *Journal of Volcanology and Geothermal Research* 458, 108264. <https://doi.org/10.1016/j.jvolgeores.2024.108264>
- Keir, D., Ebinger, C.J., Stuart, G.W., Daly, E., Ayele, A., 2006. Strain accommodation by magmatism and faulting as rifting proceeds to breakup: Seismicity of the northern Ethiopian rift. *Journal of Geophysical Research: Solid Earth* 111. <https://doi.org/10.1029/2005JB003748>
- Kiseeva, E.S., Wood, B.J., 2015. The effects of composition and temperature on chalcophile and lithophile element partitioning into magmatic sulphides. *Earth and Planetary Science Letters* 424, 280–294. <https://doi.org/10.1016/j.epsl.2015.05.012>
- Kress, V.C., Carmichael, I.S.E., 1991. The compressibility of silicate liquids containing Fe₂O₃ and the effect of composition, temperature, oxygen fugacity and pressure on their redox states. *Contr. Mineral. and Petrol.* 108, 82–92. <https://doi.org/10.1007/BF00307328>
- Lamadrid, H.M., Moore, L.R., Moncada, D., Rimstidt, J.D., Burruss, R.C., Bodnar, R.J., 2017. Reassessment of the Raman CO₂ densimeter. *Chemical Geology* 450, 210–222. <https://doi.org/10.1016/j.chemgeo.2016.12.034>
- Lerner, A.H., Muth, M.J., Wallace, P.J., Lanzirotti, A., Newville, M., Gaetani, G.A., Chowdhury, P., Dasgupta, R., 2021. Improving the reliability of Fe- and S-XANES measurements in silicate glasses: Correcting beam damage and identifying Fe-oxide nanolites in hydrous and anhydrous melt inclusions. *Chemical Geology* 586, 120610. <https://doi.org/10.1016/j.chemgeo.2021.120610>
- Lerner, A.H., O'Hara, D., Karlstrom, L., Ebmeier, S.K., Anderson, K.R., Hurwitz, S., 2020. The Prevalence and Significance of Offset Magma Reservoirs at Arc

- Volcanoes. *Geophysical Research Letters* 47, e2020GL087856.
<https://doi.org/10.1029/2020GL087856>
- Lo Forte, F.M., Schiavi, F., Rose-Koga, E.F., Rotolo, S.G., Verdier-Paoletti, M., Aiuppa, A., Zanon, V., 2024. High CO₂ in the mantle source of ocean island basanites. *Geochimica et Cosmochimica Acta* 368, 93–111.
<https://doi.org/10.1016/j.gca.2024.01.016>
- Lubbers, J., Kent, A., Russo, C., 2021. LaserTRAM-DB: A Time Resolved Analysis Module for the complete reduction of Laser Ablation Inductively Coupled Plasma Mass Spectrometry data. <https://doi.org/10.31223/X5QG95>
- Masotta, M., Mollo, S., Freda, C., Gaeta, M., Moore, G., 2013. Clinopyroxene–liquid thermometers and barometers specific to alkaline differentiated magmas. *Contrib Mineral Petrol* 166, 1545–1561. <https://doi.org/10.1007/s00410-013-0927-9>
- Métrich, N., Zanon, V., Créon, L., Hildenbrand, A., Moreira, M., & Marques, F. O. (2014). Is the ‘Azores hotspot’ a wet spot? Insights from the geochemistry of fluid and melt inclusions in olivine of Pico basalts. *Journal of Petrology*, 55(2), 377–393.
<https://doi.org/10.1093/petrology/egt071>
- Mechie, J., Keller, G. R., Prodehl, C., Khan, M. A., & Gaciri, S. J. (1997). A model for the structure, composition and evolution of the Kenya rift. *Tectonophysics*, 278(1–4), 95–119.
- Moore, L.R., Bodnar, R.J., 2019. A pedagogical approach to estimating the CO₂ budget of magmas. *JGS* 176, 398–407. <https://doi.org/10.1144/jgs2018-094>
- Muirhead, James D., Simon A. Kattenhorn, and Nicolas Le Corvec. “Varying Styles of Magmatic Strain Accommodation across the East African Rift.” *Geochemistry, Geophysics, Geosystems* 16, no. 8 (2015): 2775–95.
<https://doi.org/10.1002/2015GC005918>.
- Mutch, E.J.F., Newcombe, M.E., Rudge, J.F., 2024. 3D Diffusion of Water in Melt Inclusion-Bearing Olivine Phenocrysts. *Geochemistry, Geophysics, Geosystems* 25, e2023GC011365. <https://doi.org/10.1029/2023GC011365>
- Muth, Michelle J., and Elizabeth Cottrell. No detectable redox exchange between sulfur and iron during rapid cooling of basalts. *Earth and Planetary Science Letters* 616 (August 2023): 118210. <https://doi.org/10.1016/j.epsl.2023.118210>.

- Muth, M.J., Wallace, P.J., 2021. Slab-derived sulfate generates oxidized basaltic magmas in the southern Cascade arc (California, USA). *Geology* 49, 1177–1181.
<https://doi.org/10.1130/G48759.1>
- Nash, W.M., Smythe, D.J., Wood, B.J., 2019. Compositional and temperature effects on sulfur speciation and solubility in silicate melts. *Earth and Planetary Science Letters* 507, 187–198. <https://doi.org/10.1016/j.epsl.2018.12.006>
- Neave, D.A., Putirka, K.D., 2017. A new clinopyroxene-liquid barometer, and implications for magma storage pressures under Icelandic rift zones. *American Mineralogist* 102, 777–794. <https://doi.org/10.2138/am-2017-5968>
- Newcombe, M. E., Alessandro Fabbriozio, Youxue Zhang, C. Ma, Marion Le Voyer, Y. Guan, J. M. Eiler, A. E. Saal, and E. M. Stolper. (2014). Chemical zonation in olivine-hosted melt inclusions. *Contributions to Mineralogy and Petrology*, 168, 1-26.
- Newman, S., Lowenstern, J.B., 2002. VolatileCalc: a silicate melt–H₂O–CO₂ solution model written in Visual Basic for excel. *Computers & Geosciences* 28, 597–604.
[https://doi.org/10.1016/S0098-3004\(01\)00081-4](https://doi.org/10.1016/S0098-3004(01)00081-4)
- Newville, M., 2013. Larch: An Analysis Package for XAFS and Related Spectroscopies. *J. Phys.: Conf. Ser.* 430, 012007. <https://doi.org/10.1088/1742-6596/430/1/012007>
- O'Neill, H.St.C., 2021. The Thermodynamic Controls on Sulfide Saturation in Silicate Melts with Application to Ocean Floor Basalts, in: *Magma Redox Geochemistry*. American Geophysical Union (AGU), pp. 177–213.
<https://doi.org/10.1002/9781119473206.ch10>
- 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. <https://doi.org/10.1016/j.jafrearsci.2016.05.026>
- Rasmussen, D.J., Plank, T.A., Wallace, P.J., Newcombe, M.E., Lowenstern, J.B., 2020. Vapor-bubble growth in olivine-hosted melt inclusions. *American Mineralogist* 105, 1898–1919. <https://doi.org/10.2138/am-2020-7377>
- Rose-Koga, E.F., and 70 others, 2021. Silicate melt inclusions in the new millennium: A review of recommended practices for preparation, analysis, and data presentation.

- Chemical Geology 570, 120145.
<https://doi.org/10.1016/j.chemgeo.2021.120145>
- Schiavi, F., Bolfan-Casanova, N., Buso, R., Laumonier, M., Laporte, D., Medjoubi, K., Venugopal, S., Gómez-Ulla, A., Cluzel, N., Hardiagon, M., 2020. Quantifying magmatic volatiles by Raman microtomography of glass inclusion-hosted bubbles. *Geochem. Persp. Let.* 16, 17–24. <https://doi.org/10.7185/geochemlet.2038>
- Ryan, M. P. (1987). The elasticity and contractancy of Hawaiian olivine tholeiite, and its role in the stability and structural evolution of sub-caldera magma reservoirs and rift systems. In *Volcanism in Hawaii*. US Geol. Surv. Prof. Pap., 1350, 1395-1447.
- Shishkina, T.A., Botcharnikov, R.E., Holtz, F., Almeev, R.R., Jazwa, A.M., Jakubiak, A.A., 2014. Compositional and pressure effects on the solubility of H₂O and CO₂ in mafic melts. *Chemical Geology* 388, 112–129.
<https://doi.org/10.1016/j.chemgeo.2014.09.001>
- Saria, E., Calais, E., Stamps, D.S., Delvaux, D., Hartnady, C.J.H., 2014. Present-day kinematics of the East African Rift. *JGR Solid Earth* 119, 3584–3600.
<https://doi.org/10.1002/2013JB010901>
- Smythe, D.J., Wood, B.J., Kiseeva, E.S., 2017. The S content of silicate melts at sulfide saturation: New experiments and a model incorporating the effects of sulfide composition. *American Mineralogist* 102, 795–803. <https://doi.org/10.2138/am-2017-5800CCBY>
- Stamm, N., & Schmidt, M. W. (2017). Asthenospheric kimberlites: volatile contents and bulk compositions at 7 GPa. *Earth and Planetary Science Letters*, 474, 309-321.
<https://doi.org/10.1016/j.epsl.2017.06.037>
- Sutton, S.R., Lanzirotti, A., Newville, M., Rivers, M.L., Eng, P., Lefticariu, L., 2017. Spatially Resolved Elemental Analysis, Spectroscopy and Diffraction at the GSECARS Sector at the Advanced Photon Source. *J of Env Quality* 46, 1158–1165.
<https://doi.org/10.2134/jeq2016.10.0401>
- Sun, S., McDonough, W.F., 1989. Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes. *SP 42*, 313–345.
<https://doi.org/10.1144/GSL.SP.1989.042.01.19>

- Toplis, M.J., 2005. The thermodynamics of iron and magnesium partitioning between olivine and liquid: criteria for assessing and predicting equilibrium in natural and experimental systems. *Contrib Mineral Petrol* 149, 22–39.
<https://doi.org/10.1007/s00410-004-0629-4>
- Tuohy, R.M., Wallace, P.J., Loewen, M.W., Swanson, D.A., Kent, A.J.R., 2016. Magma transport and olivine crystallization depths in Kīlauea’s east rift zone inferred from experimentally rehomogenized melt inclusions. *Geochimica et Cosmochimica Acta* 185, 232–250. <https://doi.org/10.1016/j.gca.2016.04.020>
- Venugopal, S., Schiavi, F., Moune, S., Bolfan-Casanova, N., Druitt, T., Williams-Jones, G., 2020. Melt inclusion vapour bubbles: the hidden reservoir for major and volatile elements. *Sci Rep* 10, 9034. <https://doi.org/10.1038/s41598-020-65226-3>
- Wallace, P.J., Kamenetsky, V.S., Cervantes, P., 2015. Melt inclusion CO₂ contents, pressures of olivine crystallization, and the problem of shrinkage bubbles. *American Mineralogist* 100, 787–794. <https://doi.org/10.2138/am-2015-5029>
- Wallace, P.J., Carmichael, I.S.E., 1994. S speciation in submarine basaltic glasses as determined by measurements of SKc X-ray wavelength shifts. *American Mineralogist* 79, 161–167.
- Walowski, K.J., Wallace, P.J., Cashman, K.V., Marks, J.K., Clynne, M.A., Ruprecht, P., 2019. Understanding melt evolution and eruption dynamics of the 1666 C.E. eruption of Cinder Cone, Lassen Volcanic National Park, California: Insights from olivine-hosted melt inclusions. *Journal of Volcanology and Geothermal Research* 387, 106665. <https://doi.org/10.1016/j.jvolgeores.2019.106665>
- Wieser, P., Petrelli, M., Lubbers, J., Wieser, E., Ozaydin, S., Kent, A., Till, C., 2022. Thermobar: An open-source Python3 tool for thermobarometry and hygrometry. *Volcanica* 5, 349–384. <https://doi.org/10.30909/vol.05.02.349384>
- Wieser, P.E., Kent, A.J.R., Till, C.B., Donovan, J., Neave, D.A., Blatter, D.L., Krawczynski, M.J., 2023. Barometers Behaving Badly I: Assessing the Influence of Analytical and Experimental Uncertainty on Clinopyroxene Thermobarometry Calculations at Crustal Conditions. *Journal of Petrology* 64, egac126.

- Wilke, M., Klimm, K., Kohn, S.C., 2011. Spectroscopic Studies on Sulfur Speciation in Synthetic and Natural Glasses. *Reviews in Mineralogy and Geochemistry* 73, 41–78. <https://doi.org/10.2138/rmg.2011.73.3>
- Zhang, H.L., Cottrell, E., Solheid, P.A., Kelley, K.A., Hirschmann, M.M., 2018. Determination of $\text{Fe}^{3+}/\Sigma\text{Fe}$ of XANES basaltic glass standards by Mössbauer spectroscopy and its application to the oxidation state of iron in MORB. *Chemical Geology* 479, 166–175. <https://doi.org/10.1016/j.chemgeo.2018.01.006>

Chapter IV

- Allison CM, Roggensack K, Clarke AB (2022) MafCH: a general model for H_2O – CO_2 solubility in mafic magmas. *Contrib Mineral Petrol* 177:40. <https://doi.org/10.1007/s00410-022-01903-y>
- Aoki K-I, Yoshida T, Yusa K, Nakamura Y (1985) Petrology and geochemistry of the Nyamuragira volcano, Zaire. *Journal of Volcanology and Geothermal Research* 25:1–28. [https://doi.org/10.1016/0377-0273\(85\)90002-2](https://doi.org/10.1016/0377-0273(85)90002-2)
- Aufrère SM, Williams-Jones G, Moune S, et al (2024) Olivine Time-Capsules Constrain the Pre-Eruptive History of Holocene Basalts, Mount Meager Volcanic Complex, British Columbia, Canada. *Journal of Petrology* egae089. <https://doi.org/10.1093/petrology/egae089>
- Balagizi CM, Kies A, Kasereka MM, et al (2018) Natural hazards in Goma and the surrounding villages, East African Rift System. *Nat Hazards* 93:31–66. <https://doi.org/10.1007/s11069-018-3288-x>
- Barrière J, d'Oreye N, Smets B, et al (2022) Intra-Crater Eruption Dynamics at Nyiragongo (D.R. Congo), 2002–2021. *Journal of Geophysical Research: Solid Earth* 127:e2021JB023858. <https://doi.org/10.1029/2021JB023858>
- Barth A, Newcombe M, Plank T, et al (2019) Magma decompression rate correlates with explosivity at basaltic volcanoes — Constraints from water diffusion in olivine. *Journal of Volcanology and Geothermal Research* 387:106664. <https://doi.org/10.1016/j.jvolgeores.2019.106664>

- Barth A, Portnyagin M, Mironov N, et al (2024) Fast, furious, and gassy: Etna's explosive eruption from the mantle. *Earth and Planetary Science Letters* 643:118864.
<https://doi.org/10.1016/j.epsl.2024.118864>
- Benoît S, Christelle W (2010) A new map of the lava flow field of Nyamulagira (D.R. Congo) from satellite imagery. *Journal of African Earth Sciences*
- Biggs J, Ayele A, Fischer TP, et al (2021) Volcanic activity and hazard in the East African Rift Zone. *Nat Commun* 12:6881. <https://doi.org/10.1038/s41467-021-27166-y>
- Bobrowski N, Giuffrida GB, Arellano S, et al (2017a) Plume composition and volatile flux of Nyamulagira volcano, Democratic Republic of Congo, during birth and evolution of the lava lake, 2014–2015. *Bull Volcanol* 79:90. <https://doi.org/10.1007/s00445-017-1174-0>
- Bobrowski N, Giuffrida GB, Yalire M, et al (2017b) Multi-component gas emission measurements of the active lava lake of Nyiragongo, DR Congo. *Journal of African Earth Sciences* 134:856–865. <https://doi.org/10.1016/j.jafrearsci.2016.07.010>
- Boudoire G, Bobrowski N, Burgi P-Y, et al (2024) Magmatic Activity in Incipient Continental Break-Up as Revealed by Coupling Melt and Fluid Inclusions. *Journal of Petrology* 65:egae125. <https://doi.org/10.1093/petrology/egae125>
- Boudoire G, Giuffrida G, Liuzzo M, et al (2022) Chemical variability in volcanic gas plumes and fumaroles along the East African Rift System: New insights from the Western Branch. *Chemical Geology* 596:120811. <https://doi.org/10.1016/j.chemgeo.2022.120811>
- Brand BD, Gravley DM, Clarke AB, et al (2014a) A combined field and numerical approach to understanding dilute pyroclastic density current dynamics and hazard potential: Auckland Volcanic Field, New Zealand. *Journal of Volcanology and Geothermal Research* 276:215–232. <https://doi.org/10.1016/j.jvolgeores.2014.01.008>
- Brand BD, Gravley DM, Clarke AB, et al (2014b) A combined field and numerical approach to understanding dilute pyroclastic density current dynamics and hazard potential: Auckland Volcanic Field, New Zealand. *Journal of Volcanology and Geothermal Research* 276:215–232. <https://doi.org/10.1016/j.jvolgeores.2014.01.008>
- Burgi P -Y., Boudoire G, Rufino F, et al (2020) Recent Activity of Nyiragongo (Democratic Republic of Congo): New Insights From Field Observations and Numerical Modeling. *Geophysical Research Letters* 47:e2020GL088484.
<https://doi.org/10.1029/2020GL088484>

- Cashman KV, McConnell SM (2005) Multiple levels of magma storage during the 1980 summer eruptions of Mount St. Helens, WA. *Bull Volcanol* 68:57–75.
<https://doi.org/10.1007/s00445-005-0422-x>
- Chakrabarti R, Basu AR, Santo AP, et al (2009) Isotopic and geochemical evidence for a heterogeneous mantle plume origin of the Virunga volcanics, Western rift, East African Rift system. *Chemical Geology* 259:273–289.
<https://doi.org/10.1016/j.chemgeo.2008.11.010>
- Chakraborty S (2010) Diffusion Coefficients in Olivine, Wadsleyite and Ringwoodite. *Reviews in Mineralogy and Geochemistry* 72:603–639.
<https://doi.org/10.2138/rmg.2010.72.13>
- Couperthwaite FK, Morgan DJ, Pankhurst MJ, et al (2021) Reducing epistemic and model uncertainty in ionic inter-diffusion chronology: A 3D observation and dynamic modeling approach using olivine from Piton de la Fournaise, La Réunion. *American Mineralogist* 106:481–494. <https://doi.org/10.2138/am-2021-7296CCBY>
- Dayton K, Gazel E, Wieser P, et al (2023) Deep magma storage during the 2021 La Palma eruption. *Sci Adv* 9:eade7641. <https://doi.org/10.1126/sciadv.ade7641>
- d'Oreye N, Fernandez J, Gonzalez P, et al (2008) Systematic InSAR monitoring of African active volcanic zones: What we have learned in three years, or an harvest beyond our expectations. In: 2008 Second Workshop on Use of Remote Sensing Techniques for Monitoring Volcanoes and Seismogenic Areas. IEEE, Napoli, Italy, pp 1–6
- Demant A, Lestrade P, Lubala RT, et al (1994) Volcanological and petrological evolution of Nyiragongo volcano, Virunga volcanic field, Zaire. *Bull Volcanol* 56:47–61.
<https://doi.org/10.1007/BF00279728>
- Dohmen R, Chakraborty S (2007) Fe–Mg diffusion in olivine II: point defect chemistry, change of diffusion mechanisms and a model for calculation of diffusion coefficients in natural olivine
- Ferriss E, Plank T, Newcombe M, et al (2018) Rates of dehydration of olivines from San Carlos and Kilauea Iki. *Geochimica et Cosmochimica Acta* 242:165–190.
<https://doi.org/10.1016/j.gca.2018.08.050>

- Gavrilenko M, Batanova VG, Llovet X, et al (2023) Secondary fluorescence effect quantification of EPMA analyses of olivine grains embedded in basaltic glass. *Chemical Geology* 621:121328. <https://doi.org/10.1016/j.chemgeo.2023.121328>
- Gee, L. L., Sack, R. O. (1988). Experimental petrology of melilite nephelinites. *Journal of Petrology*, 29(6), 1233-1255.
- Girona T, Costa F (2013) DIPRA: A user-friendly program to model multi-element diffusion in olivine with applications to timescales of magmatic processes. *Geochem Geophys Geosyst* 14:422–431. <https://doi.org/10.1029/2012GC004427>
- Girona T, Realmuto V, Lundgren P (2021) Large-scale thermal unrest of volcanoes for years prior to eruption. *Nat Geosci* 14:238–241. <https://doi.org/10.1038/s41561-021-00705-4>
- Gordeychik B, Churikova T, Shea T, et al (2021) Fo and Ni Relations in Olivine Differentiate between Crystallization and Diffusion Trends. *Journal of Petrology* 61:egaa083. <https://doi.org/10.1093/petrology/egaa083>
- Hauri E, Gaetani G, Green T (2006) Partitioning of water during melting of the Earth's upper mantle at H₂O-undersaturated conditions. *Earth and Planetary Science Letters* 248:715–734. <https://doi.org/10.1016/j.epsl.2006.06.014>
- Head EM, Shaw AM, Wallace PJ, et al (2011a) Insight into volatile behavior at Nyamuragira volcano (D.R. Congo, Africa) through olivine-hosted melt inclusions. *Geochemistry, Geophysics, Geosystems* 12:. <https://doi.org/10.1029/2011GC003699>
- Head EM, Shaw AM, Wallace PJ, et al (2011b) Insight into volatile behavior at Nyamuragira volcano (D.R. Congo, Africa) through olivine-hosted melt inclusions: VOLATILE BEHAVIOR AT NYAMURAGIRA VOLCANO. *Geochem Geophys Geosyst* 12:n/a-n/a. <https://doi.org/10.1029/2011GC003699>
- Hughes EC, Biasi J, Fendley I, et al (2024) Modeling the behavior of sulfur in magmatic systems from source to surface: Application to Whakaari/White Island, Aotearoa New Zealand, and Etna, Italy. *Journal of Volcanology and Geothermal Research* 446:107939. <https://doi.org/10.1016/j.jvolgeores.2023.107939>
- Kahl M, Viccaro M, Ubide T, et al (2017) A Branched Magma Feeder System during the 1669 Eruption of Mt Etna: Evidence from a Time-integrated Study of Zoned Olivine Phenocryst Populations. *Journal of Petrology* 58:443–472. <https://doi.org/10.1093/petrology/egx022>

- Kamate Kaleghetso E, Namur O, Smets B, et al (2025) Magmatic differentiation and plumbing system beneath Nyamulagira volcano (Virunga Volcanic Province, East African Rift). *Journal of Volcanology and Geothermal Research* 458:108264.
<https://doi.org/10.1016/j.jvolgeores.2024.108264>
- Kasahara M, Tanaka K, Zana N (1991) A flank eruption of volcano Nyamuragira in 1991 -- Mikombe--. *アフリカ研究* 39:29–50
- Kervyn M, Barette F, Poppe S, et al (2024) Assessing lava flow susceptibility at neighbouring volcanoes: Nyamulagira and Nyiragongo volcanoes, Virunga Volcanic Province. *J Appl Volcanol* 13:5. <https://doi.org/10.1186/s13617-024-00143-y>
- Kling G, Clark M, Compton D, et al (2025) The 1986 Lake Nyos Gas Disaster in Cameroon, West Africa. *Science* 236:169–175
- Komorowski J-C, Tedesco D, Kasereka M, et al (2002) The January 2002 Flank Eruption Of Nyiragongo Volcano (Democratic Republic Of Congo): Chronology, Evidence For A Tectonic Rift Trigger, And Impact Of Lava Flows On The City Of Goma
- Kyambikwa A, Ebinger CJ, Kalugana C, et al (2024) Pre-Eruption Seismicity Associated with the May 2021 Eruption of Nyiragongo Volcano, Kivu Rift. Washington, D.C.
- Laumonier M, Laporte D, Faure F, et al (2019) An experimental study of dissolution and precipitation of forsterite in a thermal gradient: implications for cellular growth of olivine phenocrysts in basalt and melt inclusion formation. *Contrib Mineral Petrol* 174:94.
<https://doi.org/10.1007/s00410-019-1627-x>
- Lerner AH, Wallace PJ, Shea T, et al (2021) The petrologic and degassing behavior of sulfur and other magmatic volatiles from the 2018 eruption of Kīlauea, Hawai‘i: melt concentrations, magma storage depths, and magma recycling. *Bull Volcanol* 83:43.
<https://doi.org/10.1007/s00445-021-01459-y>
- Lynn KJ, Liliana, DeSmither G. (2023) US Geological Survey Techniques and Methods. In: *Creating Oriented and Precisely Sectioned Mineral Mounts for In Situ Chemical Analyses—An Example Using Olivine for Diffusion Chronometry Studies*
- Lynn KJ, Nadeau PA, Ruth DCS, et al (2024) Olivine diffusion constrains months-scale magma transport within Kīlauea volcano’s summit reservoir system prior to the 2020 eruption. *Bull Volcanol* 86:31. <https://doi.org/10.1007/s00445-024-01714-y>

- Mafuko-Nyandwi B, Kervyn M, Habiwaremye FM, et al (2024) Building a prepared community to volcanic risk in the global south: Assessment of awareness raising tools for high school students in Goma, (East DR Congo). *Progress in Disaster Science* 24:100370. <https://doi.org/10.1016/j.pdisas.2024.100370>
- Martin VM, Morgan DJ, Jerram DA, et al (2008) Bang! Month-Scale Eruption Triggering at Santorini Volcano. *Science* 321:1178–1178. <https://doi.org/10.1126/science.1159584>
- Matzen AK, Baker MB, Beckett JR, Stolper EM (2011) Fe–Mg Partitioning between Olivine and High-magnesian Melts and the Nature of Hawaiian Parental Liquids. *Journal of Petrology* 52:1243–1263. <https://doi.org/10.1093/petrology/egq089>
- Mavonga T, Zana N, Durrheim RJ (2010) Studies of crustal structure, seismic precursors to volcanic eruptions and earthquake hazard in the eastern provinces of the Democratic Republic of Congo. *Journal of African Earth Sciences* 58:623–633. <https://doi.org/10.1016/j.jafrearsci.2010.08.008>
- Mavonga T, Kavotha SK, Lukaya N, et al (2006) Seismic activity prior to the May 8, 2004 eruption of volcano Nyamuragira, Western Rift Valley of Africa. *Journal of Volcanology and Geothermal Research* 158:355–360. <https://doi.org/10.1016/j.jvolgeores.2006.06.021>
- Michellier C, Kervyn M, Barette F, et al (2020) Evaluating population vulnerability to volcanic risk in a data scarcity context: The case of Goma city, Virunga volcanic province (DR Congo). *International Journal of Disaster Risk Reduction* 45:101460. <https://doi.org/10.1016/j.ijdrr.2019.101460>
- Minissale S, Casalini M, Cucciniello C, et al (2022) The geochemistry of recent Nyamulagira and Nyiragongo potassic lavas, Virunga Volcanic Province, and implications on the enrichment processes in the mantle lithosphere of the Tanzania-Congo craton. *Lithos* 420–421:106696. <https://doi.org/10.1016/j.lithos.2022.106696>
- Minissale S, Zanetti A, Tedesco D, et al (2019) The petrology and geochemistry of Nyiragongo lavas of 2002, 2016, 1977 and 2017 AD, and the trace element partitioning between melilitite glass and melilite, nepheline, leucite, clinopyroxene, apatite, olivine and Fe-Ti oxides: a unique scenario. *Lithos* 332–333:296–311. <https://doi.org/10.1016/j.lithos.2019.02.023>

- Molendijk SM, Namur O, Kamate Kaleghetso E, et al (2024) Plumbing System Architecture and Differentiation Processes of the Nyiragongo Volcano, DR Congo. *Journal of Petrology* 65:egad088. <https://doi.org/10.1093/petrology/egad088>
- Molendijk SM, Namur O, Mason PRD, et al (2023) Trace element partitioning in silica-undersaturated alkaline magmatic systems. *Geochimica et Cosmochimica Acta* 346:29–53. <https://doi.org/10.1016/j.gca.2023.01.025>
- Mourey AJ, Shea T, Costa F, et al (2023) Years of magma intrusion primed Kīlauea Volcano (Hawai'i) for the 2018 eruption: evidence from olivine diffusion chronometry and monitoring data. *Bull Volcanol* 85:18. <https://doi.org/10.1007/s00445-023-01633-4>
- Muhindo Syavulisembo A, Kervyn F, Lennert M, et al (2024) Assessing accessibility to critical resources for volcanic risk management in Goma, Democratic Republic of Congo. *Volcanica* 7:871–890. <https://doi.org/10.30909/vol.07.02.871890>
- Newcombe ME, Plank T, Barth A, et al (2020) Water-in-olivine magma ascent chronometry: Every crystal is a clock. *Journal of Volcanology and Geothermal Research* 398:106872. <https://doi.org/10.1016/j.jvolgeores.2020.106872>
- Phillips EH, Sims KWW, Blichert-Toft J, et al Mantle sources, eruptive cyclicality, and magmatic evolution at Nyiragongo and Nyamulagira Volcanoes, Virunga Volcanic Province, DR Congo
- Platz T, Foley SF, André L (2004) Low-pressure fractionation of the Nyiragongo volcanic rocks, Virunga Province, D.R. Congo. *Journal of Volcanology and Geothermal Research* 136:269–295. <https://doi.org/10.1016/j.jvolgeores.2004.05.020>
- Poppe S, Smets B, Fontijn K, et al (2016) Holocene phreatomagmatic eruptions alongside the densely populated northern shoreline of Lake Kivu, East African Rift: timing and hazard implications. *Bull Volcanol* 78:82. <https://doi.org/10.1007/s00445-016-1074-8>
- Pouclet A (1976) *Volcanologie Du Rift De L’afrique Centrale Le Nyamuragira Dans Les Virunga Essai De Magmatologie Du Rift*. Universite de Paris-Sud
- Pouclet A, Bram K (2021) Nyiragongo and Nyamuragira: a review of volcanic activity in the Kivu rift, western branch of the East African Rift System. *Bull Volcanol* 83:10. <https://doi.org/10.1007/s00445-021-01435-6>
- Putirka K (2016) Rates and styles of planetary cooling on Earth, Moon, Mars, and Vesta, using new models for oxygen fugacity, ferric-ferrous ratios, olivine-liquid Fe-Mg

- exchange, and mantle potential temperature. *American Mineralogist* 101:819–840.
<https://doi.org/10.2138/am-2016-5402>
- Putirka KD (2008) Thermometers and Barometers for Volcanic Systems. *Reviews in Mineralogy and Geochemistry* 69:61–120. <https://doi.org/10.2138/rmg.2008.69.3>
- Ruth DCS, Costa F, Bouvet De Maisonneuve C, et al (2018) Crystal and melt inclusion timescales reveal the evolution of magma migration before eruption. *Nat Commun* 9:2657. <https://doi.org/10.1038/s41467-018-05086-8>
- Sahama TG, Meyer (1958) A Study Of The Volcano Nyiragongo A Progress Report
- Sawyer GM, Carn SA, Tsanev VI, et al (2008) Investigation into magma degassing at Nyiragongo volcano, Democratic Republic of the Congo: Magma Degassing At Nyiragongo Volcano. *Geochem Geophys Geosyst* 9:n/a-n/a.
<https://doi.org/10.1029/2007GC001829>
- Schneider CA, Rasband WS, Eliceiri KW (2012) NIH Image to ImageJ: 25 years of image analysis. *Nat Methods* 9:671–675. <https://doi.org/10.1038/nmeth.2089>
- Shea T, Hammer JE, Hellebrand E, et al (2019) Phosphorus and aluminum zoning in olivine: contrasting behavior of two nominally incompatible trace elements. *Contrib Mineral Petrol* 174:85. <https://doi.org/10.1007/s00410-019-1618-y>
- Shea T, K. Matzen A, J. Mourey A (2022) Experimental study of Fe–Mg partitioning and zoning during rapid growth of olivine in Hawaiian tholeiites. *Contrib Mineral Petrol* 177:114. <https://doi.org/10.1007/s00410-022-01969-8>
- Shea T, Lynn KJ, Garcia MO (2015) Cracking the olivine zoning code: Distinguishing between crystal growth and diffusion. *Geology* 43:935–938.
<https://doi.org/10.1130/G37082.1>
- Shea T, Ruth D, Jollands M, et al (2023) The presence of silicate melt may enhance rates of cation diffusion in olivine. *Earth and Planetary Science Letters* 621:118370.
<https://doi.org/10.1016/j.epsl.2023.118370>
- Smets B, d'Oreye N, Kervyn F, et al (2014) Detailed multidisciplinary monitoring reveals pre- and co-eruptive signals at Nyamulagira volcano (North Kivu, Democratic Republic of Congo). *Bull Volcanol* 76:787. <https://doi.org/10.1007/s00445-013-0787-1>
- Smets B, Kervyn M, d'Oreye N, Kervyn F (2015) Spatio-temporal dynamics of eruptions in a youthful extensional setting: Insights from Nyamulagira Volcano (D.R. Congo), in the

- western branch of the East African Rift. *Earth-Science Reviews* 150:305–328.
<https://doi.org/10.1016/j.earscirev.2015.08.008>
- Smittarello D, Smets B, Barrière J, et al (2022) Precursor-free eruption triggered by edifice rupture at Nyiragongo volcano. *Nature* 609:83–88. <https://doi.org/10.1038/s41586-022-05047-8>
- Subira J Seismicity and Seismological Models of the Virunga Volcanic Province and Kivu Rift, Democratic Republic of Congo
- Tanaka K (1983) Seismicity and focal mechanism of the volcanic earthquakes in the Virunga Volcanic Region. In: Hamagushi H (ed) *Volcanoes Nyiragongo and Nyamuragira: Geophysical Aspects*. Tohoku University, Sendai, pp 19–28
- Tazieff H, (1985) Recent Activity at Nyiragongo And Lava-Lake Occurrences, Geological Society of Finland
- Tedesco D, Vaselli O, Papale P, et al (2007) January 2002 volcano-tectonic eruption of Nyiragongo volcano, Democratic Republic of Congo. *J Geophys Res* 112:2006JB004762. <https://doi.org/10.1029/2006JB004762>
- Towbin WH, Plank T, Klein E, Hauri E (2023) Measuring H₂O concentrations in olivine by secondary ion mass spectrometry: Challenges and paths forward. *American Mineralogist: Journal of Earth and Planetary Materials* 108:928–940. <https://doi.org/10.2138/am-2022-8247>
- Wadge G, Biggs J, Lloyd R, Kendall J-M (2016) Historical Volcanism and the State of Stress in the East African Rift System. *Front Earth Sci* 4:.
<https://doi.org/10.3389/feart.2016.00086>
- Wallace G, Bergantz G (2004) Constraints on mingling of crystal populations from off-center zoning profiles: a statistical approach. 89:64–73
- Wallace PA, Otieno V, Godec P, et al (2025) Temporal and spatial evolution of explosive silicic peralkaline eruptions at the Olkaria Volcanic Complex and Longonot volcano in the Southern Kenya Rift. *Journal of Volcanology and Geothermal Research* 460:108275. <https://doi.org/10.1016/j.jvolgeores.2025.108275>
- Walwer D, Wauthier C, Barrière J, et al (2023) Modeling the intermittent lava lake drops occurring between 2015 and 2021 at Nyiragongo Volcano. *Geophysical Research Letters* 50:e2022GL102365. <https://doi.org/10.1029/2022GL102365>

- Wauthier C, Cayol V, Kervyn F, d'Oreye N (2012) Magma sources involved in the 2002 Nyiragongo eruption, as inferred from an InSAR analysis. *Journal of Geophysical Research: Solid Earth* 117:. <https://doi.org/10.1029/2011JB008257>
- Wauthier C, Cayol V, Poland M, et al (2013) Nyamulagira's magma plumbing system inferred from 15 years of InSAR. *SP* 380:39–65. <https://doi.org/10.1144/SP380.9>
- Wauthier C, Cayol V, Smets B, et al (2015) Magma Pathways and Their Interactions Inferred from InSAR and Stress Modeling at Nyamulagira Volcano, D.R. Congo. *Remote Sensing* 7:15179–15202. <https://doi.org/10.3390/rs71115179>
- Welsch B, Faure F, First EC (2023a) Reappraising Crystallization Kinetics with Overgrowth Chronometry: an *in Situ* Study of Olivine Growth Velocities. *Journal of Petrology* 64:egad055. <https://doi.org/10.1093/petrology/egad055>
- Welsch B, Faure F, First EC (2023b) Reappraising Crystallization Kinetics with Overgrowth Chronometry: an *in Situ* Study of Olivine Growth Velocities. *Journal of Petrology* 64:egad055. <https://doi.org/10.1093/petrology/egad055>
- Wood DA, Scholz CA (2017) Stratigraphic framework and lake level history of Lake Kivu, East African Rift. *Journal of African Earth Sciences* 134:904–916. <https://doi.org/10.1016/j.jafrearsci.2016.06.014>
- Zana N, Tanaka K, Kasahara M, et al Observations of Volcanic Earthquakes and Tremors at Volcanoes Nyiragongo and Nyamuragira in the Western Rift Valley of Africa