

THESIS

THE HAWAIIAN MELTING POT BENEATH KO‘OLAU VOLCANO, O‘AHU: CRYSTAL
RECORD EVIDENCE OF SILICIC MELT MIXING

Submitted by

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In partial fulfillment of the requirements

For the degree of Master of Science

Colorado State University

Fort Collins, Colorado

Summer 2026

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ABSTRACT

THE HAWAIIAN MELTING POT BENEATH KO‘OLAU VOLCANO, O‘AHU: CRYSTAL RECORD EVIDENCE OF SILICIC MELT MIXING

The Hawaiian-Emperor chain is an alignment of 129 volcanoes in the Pacific Ocean, formed as the Pacific Plate moves across the Hawaiian Mantle Plume. Since ~5 Ma, it has developed two spatially organized mantle geochemical signatures: Loa-type volcanoes on the southwestern side of the chain and Kea-type volcanoes on the northeastern, defined by distinct isotopic and trace element compositions. Ko‘olau, a Loa-type volcano on O‘ahu, began erupting isotopically enriched lavas at the end of the shield volcanic stage (Ko‘olau-Makapu‘u). This “Enriched Loa” geochemical endmember comprises higher $^{208}\text{Pb}/^{206}\text{Pb}$, $^{87}\text{Sr}/^{86}\text{Sr}$, and SiO_2 and lower $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, CaO and TiO_2 compared to other Loa- and Kea-type lavas, which suggests distinct, time-integrated compositional variations in the magmatic source that may require non-peridotite lithologies such as pyroxenite or eclogite. Ko‘olau also is one of only two Hawaiian Island volcanoes that lacks a postshield volcanic stage, implying a potential magmatic plumbing system response to these variations in mantle source composition. The investigation of a geologically constrained stratigraphic sequence of ~0.22 Ma of eruptive history of Ko‘olau-Makapu‘u reveals physical and chemical evidence of a complex history of magma mixing. The presence of orthopyroxene reaction rims, cyclic enrichment and depletion of the Ko‘olau-Makapu‘u isotopic signature, cyclic increase and decrease in olivine and orthopyroxene crystallization temperatures, olivine Fo, and pyroxene Mg#, and complex pyroxene chemical zoning provides evidence that Ko‘olau-Makapu‘u cyclically rejuvenated the plumbing system at least three times and heavily reacted with the partially fractionated Loa-type cumulate mush in

the shallow magma storage reservoir. This study provides a model for the petrogenesis of Ko‘olau-Makapu‘u basalts and evolution of Ko‘olau volcano from the shield to late shield informed by textural analysis of mineral populations, mineral chemistry, olivine and orthopyroxene thermometry, and Pb-Nd-Sr-Hf isotopic signatures.

ACKNOWLEDGEMENTS

I would like to give my warmest thanks to the many people who made this thesis possible. First and foremost, this endeavor would not have been possible without the support of my family. Words cannot express my gratitude for their encouragement and inspiration to pursue higher education. I also extend a warm thank you to Ally Moore, Julia Ziepfel, Kelley Dunn, Tori Dusing, and the community of Geoscience graduate students at CSU, whose distractions from my work were welcomed and kept me motivated to complete this research.

Next, I would like to thank my advisor, Dr. Lauren Harrison, and my committee members, Dr. John Ridley and Dr. Justin Sambur, for providing me the opportunity to grow as a geoscientist at Colorado State University. Thank you for the riveting discussions, guidance, and support that shaped both this research and my professional development.

I would like to extend a huge thank you to Dr. Danny Coulthard for the many engaging and insightful discussions on electron microprobe methods and Hawaiian geology. Your expertise and willingness to share your knowledge was invaluable to this research and the completion of this thesis. Furthermore, I would like to thank Finn Rolstad for assistance in WEKA phase mapping methods development and data processing.

I would also like to extend my deepest gratitude to my colleagues, Alex Hammerstrom, Maggie Moss, and Phillip Kondracki, whose countless geochemistry and petrology discussions helped shape and advance this project forward. Whether it be talking through data interpretations or simply providing encouraging words, your support and friendship is something I will cherish forever.

I would like to extend a special thank you to Drew White. Your perseverance and curiosity have been a constant source of inspiration throughout this journey. Thank you for the late nights in the office, evening walks around the ponds with The Lady Jessica, and providing peace and perspective during the darkest times of this process. Your companionship has meant more to me than I can adequately express. I could not have asked for a better colleague and friend to share this experience with.

Lastly, I respectfully acknowledge that this work was conducted on rocks from the island of O‘ahu, the ancestral and present-day lands of the Native Hawaiian people. I recognize and honor the relationship between the Kānaka Maoli with these lavas, and I am grateful for the opportunity to learn and conduct research on Ko‘olau Volcano. Mahalo nui loa.

DEDICATION

I would like to dedicate this thesis to my nieces, nephews, and cousins: G, Bub, Evie, Makayla, Jacks, and Ari, and all the little ones to come. You keep me curious and bring so much love, joy, and purpose into my life. Thank you.

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CHAPTER 1 – INTRODUCTION

1.1 Hawaiian Geologic Background & Introduction to Geochemical Endmembers

The Hawaiian-Emperor Chain is an alignment of 129 volcanic islands in the Pacific Ocean, formed as the Pacific Plate moves over the stationary Hawaiian Mantle plume (Clague & Sherrod, 2014). Volcanoes range in age from ~80 Ma to the presently erupting Kama‘euhakanaloa Seamount (previously known as Lō‘ihi), with a prominent bend occurring around 55 Ma – 45 Ma (Sharp & Clague, 2006). The Hawaiian-Emperor chain can be divided into three sections of volcanoes: the Emperor Seamounts, the Northwestern Hawaiian Ridge (NWHR), and the Hawaiian Islands (Figure 1). The Emperor Seamounts consist of volcanoes formed >81 – 47 Ma, from the northwestern Pacific Ocean to the bend in the chain (Clague & Dalrymple, 1987). The Northwestern Hawaiian Ridge consist of volcanoes formed over the next ~42 Ma between the bend and the Hawaiian Islands (Clague & Dalrymple, 1987). Finally, the Hawaiian Islands span from 6.5 Ma to presently erupting Kīlauea and Kama‘euhakanaloa volcanoes on the Big Island (Figure 1). The Hawaiian-Emperor Chain has the highest buoyancy flux (Sleep, 1990; Wessel, 2016) and volumetric output (Robinson & Eakins, 2006), making it the archetype for ocean-island basalts (OIBs) and one of the most extensively studied mantle plumes on Earth.

Hawaiian volcanoes follow a life cycle consisting of a pre-shield, shield, post-shield, and rejuvenated stage, which represent the variety in the amount and rate of heat supplied to the lithosphere from the Hawaiian hot spot (Clague & Sherrod, 2014). The pre-shield stage is the earliest growth stage of a Hawaiian volcano and is dominated by alkalic lavas and low-degree melts. The shield stage, where 80-95% of the volcano’s volume is erupted, marks the point where

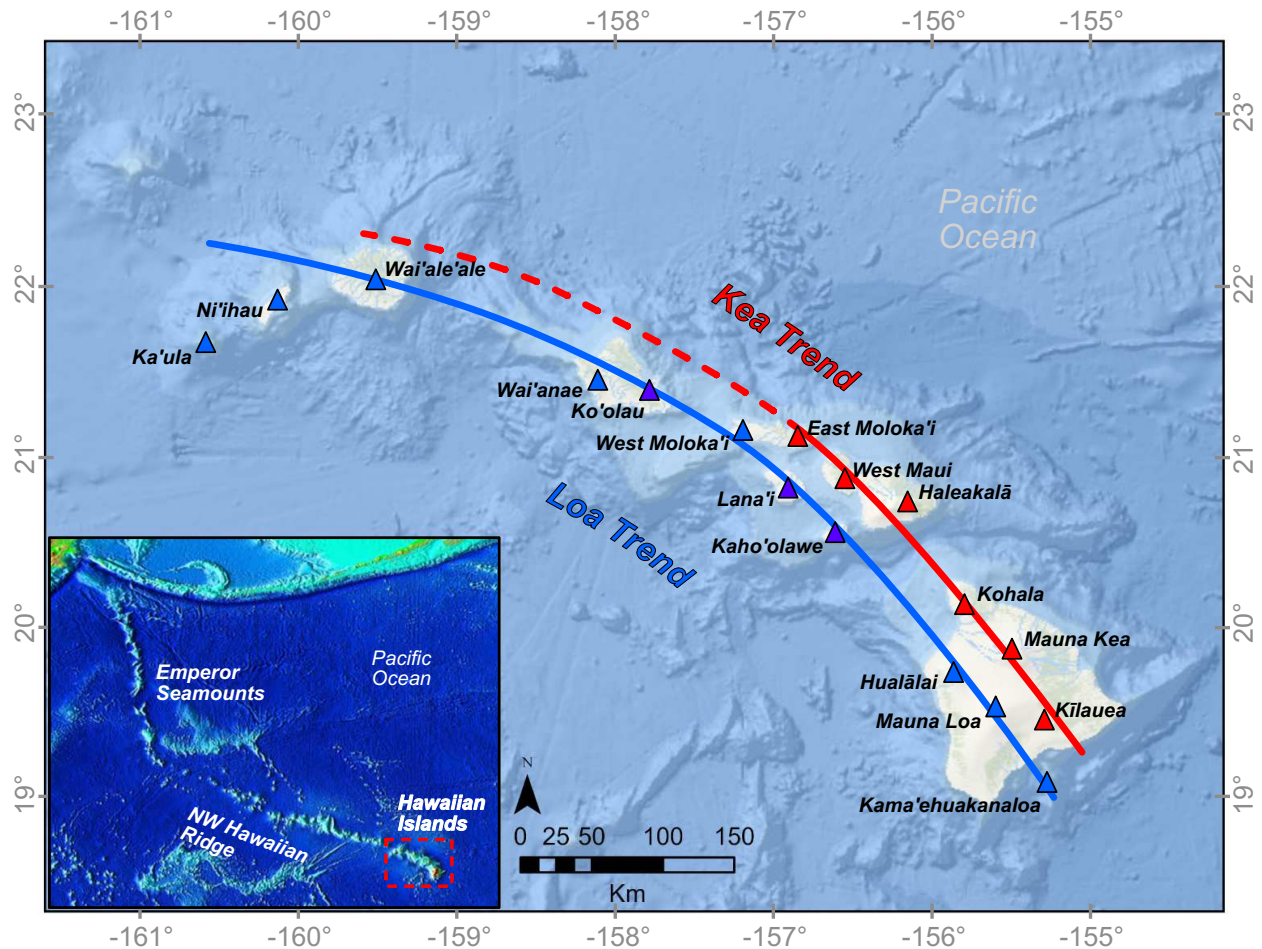


Figure 1: Map of Hawaiian Islands showing approximate locations of volcanoes and Loa- and Kea- trend tracks (blue for Loa-trend, red for Kea-trend, purple for Enriched Loa volcanoes). Inset shows bathymetric map depicting the entire Hawaiian-Emperor chain.

the volcano is near the hot spot, magma supply is plentiful, and there are high-degree melts (Clague & Sherrod, 2014). The shield stage is dominated by tholeiitic lavas and shows the largest range of isotopic variation between Hawaiian volcanoes (Abouchami et al., 2005; Tanaka et al., 2002; Weis et al., 2011; Williamson et al., 2025). The transition between pre-shield and shield stage can have interbedded alkalic and tholeiitic deposits (Clague & Sherrod, 2014). The post-shield stage occurs as the plate moves away from the hot spot, magma supply wanes, and there are low-degree melts. This stage is dominated by a mixture of tholeiitic and alkalic basalts and is consistently more isotopically depleted than shield-stage basalts (Clague & Sherrod, 2014). The

last stage of a Hawaiian volcano's life cycle is the rejuvenated stage, dominated by silica undersaturated alkalic basalts (Clague & Sherrod, 2014). These basalts represent low-degree melts, are the most isotopically depleted, and represent the most limited range of isotopic composition between volcanoes.

The Hawaiian Islands have historically been divided into two geographically organized geochemical groups, the Loa- and Kea-trend (Figure 1), which are best differentiated by $^{208}\text{Pb}/^{206}\text{Pb}$ ($((^{208}\text{Pb}/^{204}\text{Pb} - 29.476)/(^{206}\text{Pb}/^{204}\text{Pb} - 9.307))$) (Abouchami et al., 2005) as well as $^{87}\text{Sr}/^{86}\text{Sr}$, $^{176}\text{Hf}/^{177}\text{Hf}$, and $^{143}\text{Nd}/^{144}\text{Nd}$ (Williamson et al., 2025) among shield stage lavas (Figure 2). The Kea-trend, characterized by PREMA (prevalent mantle) like compositions, is prevalent along the entirety of the Hawaiian-Emperor chain (Harrison & Weis, 2018). The Loa-trend, characterized by higher Th/U and $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$, is only observed beginning at ~47 Ma at Daikakuji Volcano (Regelous et al., 2003). Generally, the Loa-trend volcanoes are concentrated along the southwest side of the chain, while the Kea-trend volcanoes are concentrated along the northeast side of the chain (Figure 1). However, there exists another geochemical trend with distinct radiogenic isotope differences relative to other Kea- and Loa- trend volcanoes: the Enriched Loa geochemical endmember, present among the Hawaiian Islands in only Ko'olau, Lāna'i, and Kaho'olawe (Figure 1 and 2). The Enriched Loa geochemical component present at Ko'olau Volcano (henceforth referred to as Ko'olau-Makapu'u) is the focus of this study.

1.2 The Enriched Loa Geochemical Endmember

The Enriched Loa geochemical endmember consists of shield stage lavas with high $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ (Figure 2), as well as high SiO_2 (Figure 3), low CaO and TiO_2 , and low incompatible trace element concentrations relative to

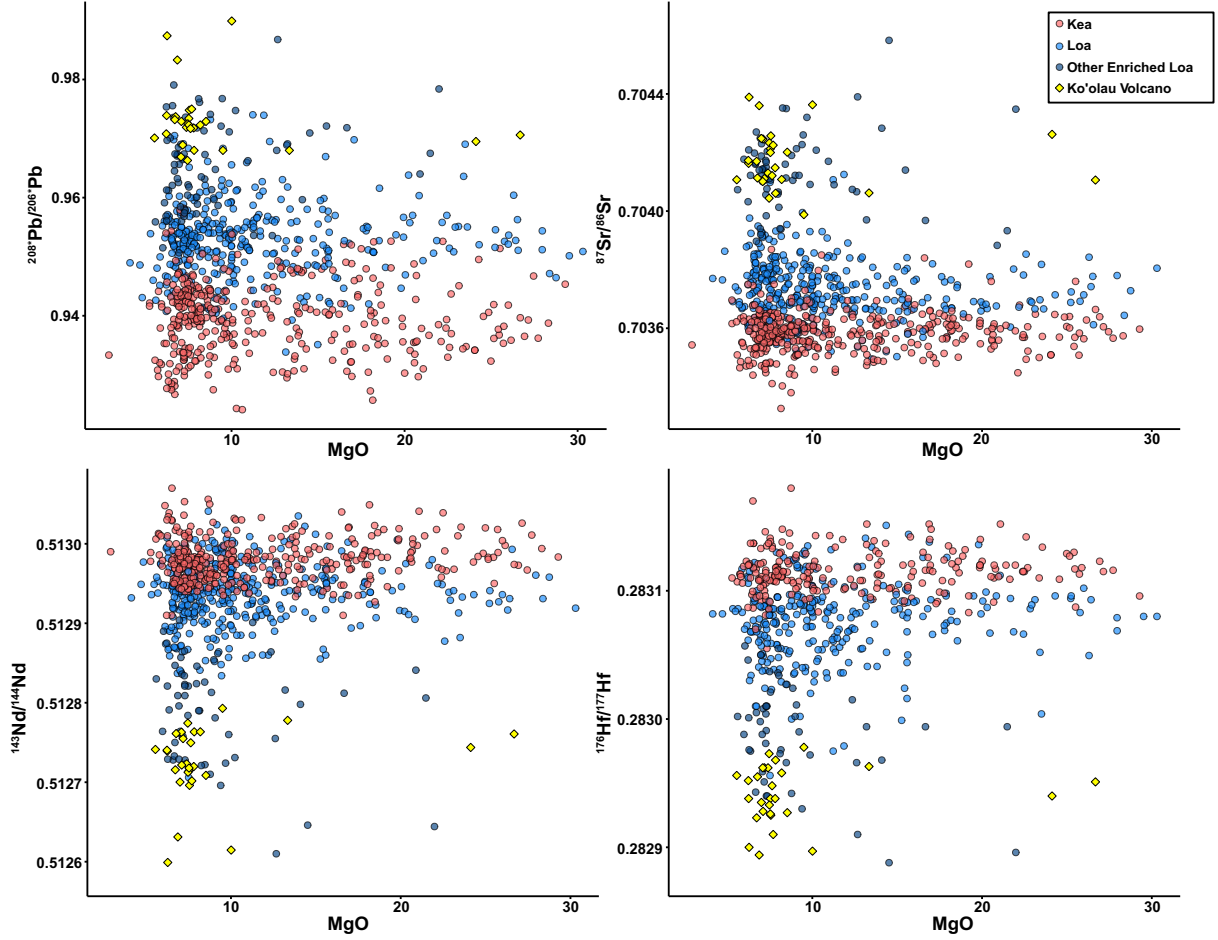


Figure 2: Radiogenic Pb-Sr-Nd-Hf isotope ratios vs. MgO, in weight %, for shield stage Kea, Loa, and Enriched Loa geochemical endmembers (database from Williamson et al., 2025). Other Enriched Loa volcanoes consists of Lāna‘i and Kaho‘olawe.

other Kea- and Loa-trend volcanoes within the Hawaiian chain (Haskins & Garcia, 2004; Jackson et al., 2012; Williamson et al., 2025). In fact, shield stage Enriched Loa volcanoes dominantly erupt basaltic andesites, rather than the basaltic compositions observed at other Kea- and Loa-type volcanoes (Figure 3). Within the Hawaiian Islands, the Enriched Loa composition first erupted on Ko‘olau Volcano at ~2.6 Ma (Yamasaki et al., 2011) and last erupted at the end of Kaho‘olawe’s shield stage at ~1.2 Ma (Fodor et al., 1992). In total, the Enriched Loa component is only observed on three volcanoes in the Hawaiian Islands: the end of the shield stage of

Ko‘olau (Ko‘olau-Makapu‘u), Lāna‘i , and Kaho‘olawe (Williamson et al., 2025). Furthermore, Enriched Loa volcanoes are unique in that they contain the only volcanoes that lack a postshield volcanic stage in all the Hawaiian Islands: Ko‘olau and Lāna‘i (Clague & Sherrod, 2014).

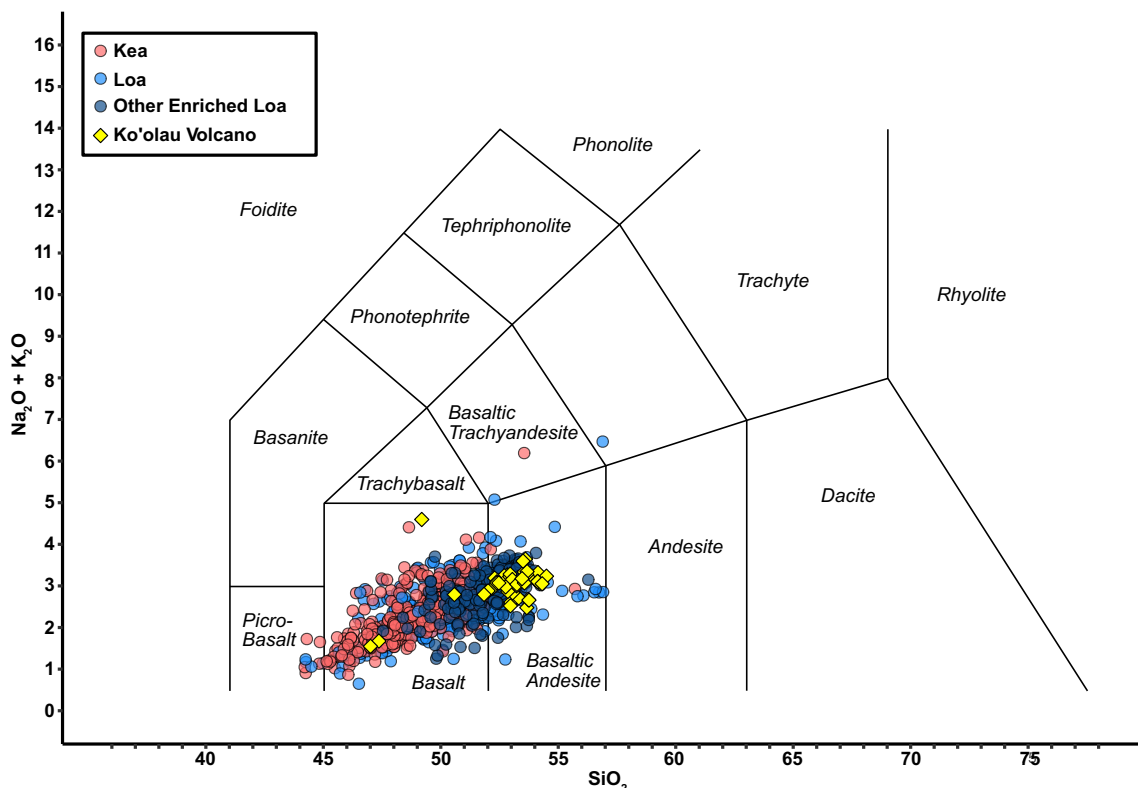


Figure 3: Total alkalis vs. silica (TAS) plot for shield stage Kea, Loa, and Enriched Loa geochemical endmembers (database from Williamson et al., 2025). Other Enriched Loa volcanoes consist of Lāna‘i and Kaho‘olawe.

However, geochemical heterogeneity exists within the Enriched Loa component itself. Despite its remarkably low volumetric output within the Hawaiian Islands (<6%), the Enriched Loa component comprises 61% of the variety in $^{208}\text{Pb}/^{206}\text{Pb}$, 27% of the variety of $^{87}\text{Sr}/^{86}\text{Sr}$, 69% of the variety of $^{143}\text{Nd}/^{144}\text{Nd}$, and 66% of the variety of $^{176}\text{Hf}/^{177}\text{Hf}$ within the entire Hawaiian chain (Williamson et al., 2025). Ko‘olau lavas have the highest $^{208}\text{Pb}/^{206}\text{Pb}$ and lowest $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ and is considered the type locality and peak expression of the Enriched Loa component (Williamson et al., 2025). Lāna‘i erupts lavas with the highest $^{87}\text{Sr}/^{86}\text{Sr}$

of the three Enriched Loa volcanoes (Williamson et al., 2025). Kaho‘olawe erupts lavas with the lowest isotopic enrichment of the three Enriched Loa volcanoes, and it also has the smallest range of isotopic concentrations, thus forming a tighter cluster of data in isotope space (Williamson et al., 2025).

There have been extensive whole-rock major and trace element (Frey et al., 1994, 2016; Haskins & Garcia, 2004; Jackson et al., 2012; Roden et al., 1984; Tanaka et al., 2002) and isotopic (Fekiacova et al., 2007; Huang & Frey, 2005; Roden et al., 1994; Weis et al., 2020; Williamson et al., 2025) studies on Enriched Loa volcanics that have attempted to explain the observed geochemical differences relative to other Hawaiian volcanoes in the context of mantle source heterogeneity. It is suggested that the Enriched Loa geochemical endmember arises from subducted oceanic material, pelagic sediments, and/or carbonates, which react with the ambient peridotite mantle to create a pyroxenite or eclogite (Blichert-Toft et al., 1999; Hauri, 1996; Huang & Frey, 2005; Jackson et al., 2012; Roden et al., 1994; Sobolev et al., 2005, 2007; Williamson et al., 2025). This pyroxenite or eclogite melts, along with surrounding peridotite mantle material that is thought to be the source for most Hawaiian parental magmas (Jackson et al., 2012). These two melts mix, likely with a larger proportion of eclogite or pyroxenite melt relative to other Hawaiian volcanoes, to create the Enriched Loa geochemical signature (Sobolev et al., 2007; Williamson et al., 2025). Indeed, some of these studies have generally described the petrography of Enriched Loa lavas, however, the emphasis lies within the interpretation of whole-rock major element, trace element, and Pb-Sr-Nd-Hf isotopic concentrations. No study currently exists that focuses on the petrography of Enriched Loa lavas or interprets any shallow-crustal plumbing system changes that may arise in response to a more enriched mantle source. Likewise, no study has attempted to explain the lack of a postshield stage among Enriched Loa

volcanoes. This study will be the first of its kind to investigate the petrographic response to a geochemically distinct mantle source material and propose a mechanism for the lack of a postshield stage at the peak expression and type locality for Enriched Loa volcanics: Ko‘olau Volcano, O‘ahu.

1.3 Ko‘olau Volcano Geologic History

The island of O‘ahu contains two extinct volcanoes: Wai‘anae, an older, Loa-type volcano located on the western side of the island, and Ko‘olau, a younger, Enriched Loa volcano located on the east. Ko‘olau Volcano’s shield stage began ~3.3 Ma, lasting for ~1.2 million years until ~2.1 Ma (Figure 4A) (Yamasaki et al., 2011). Likely near the end of shield stage volcanism, the Nu‘uanu landslide displaced $2.9\text{--}3.8 \times 10^3 \text{ km}^3$ of the eastern flank of Ko‘olau Volcano, effectively removing ~40% of the volcano, depicted in Figure 4B (Moore et al., 1989; Satake et al., 2002). Ko‘olau Volcano had no postshield stage, or alkalic cap, a unique feature to Ko‘olau and the neighboring Lāna‘i Volcano. Instead, after ~1 Ma of erosion and a hiatus of volcanic activity, its rejuvenated stage, lasting from 0.8 Ma – 0.03 Ma, produced ~40 monogenetic eruptions known as the Honolulu Volcanics (Gramlich & Naughton, 1972; Lanphere & Dalrymple, 1980; Ozawa et al., 2005).

Today, the Ko‘olau Range spans NW-SE along the eastern side of O‘ahu with the ~40 km long Nu‘uanu Pali, formed by the Nu‘uanu landslide and continuous wave-driven erosion (Wentworth & Winchell, 1947). Ko‘olau-Makapu‘u stage lavas at Makapu‘u Head (Figure 4C), rejuvenated stage Honolulu Volcanics (e.g. Diamond Head, Koko Head, Punchbowl Crater), and abundant mafic dikes are currently exposed. The mafic dikes, called the Ko‘olau dike complex, are nearly vertical and follow a NW-SE axis, which is interpreted as evidence of a long NW-SE rift zone (Figure 4A) (Wentworth and Winchell, 1947; Clague and Dalrymple, 1987). The caldera

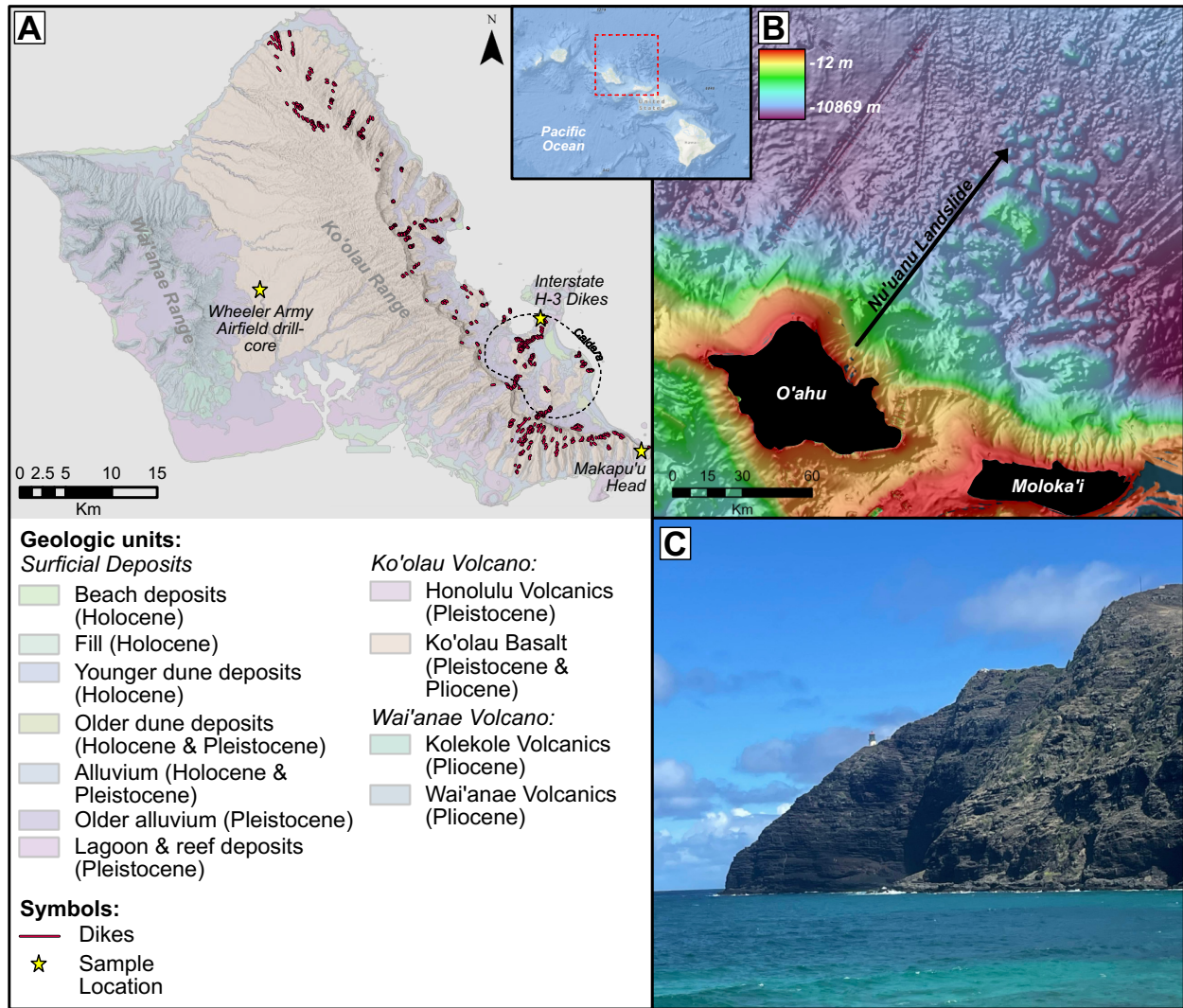


Figure 4: Maps of O'ahu showing A) simplified geologic map (from Sherrod et al., 2021) with sample locations, dike complex, and proposed caldera location. B) bathymetric map of Nu'uano Landslide deposit northeast of O'ahu. Bathymetry data from NOAA bathymetry data viewer. C) view of Makapu'u Head cliff-face looking south-southeast. Top inset map shows the Hawaiian islands with red box indicating the area depicted in panels A and B.

is thought to be located near Kāne'ōhe Bay, because of the presence of the Kailua Member basalts, which are shield stage Ko'olau basalts that are Loa-type in composition (Figure 4A) (Clague and Dalrymple, 1987). Due to the limited subaerial exposure of shield stage lavas and extensive tropical vegetative cover of most of the volcano, subaquatic samples displaced by the Nu'uano Landslide, available drill-cores (e.g. Wheeler Army Airfield Drill-core, Ko'olau

Scientific Drilling Project), or Makapu‘u Head are the best available sample locations for shield stage lavas (Garcia, 2002; Haskins & Garcia, 2004; Weinstein et al., 2004). The best exposure of Ko‘olau-Makapu‘u lavas is the ~0.22 Ma eruptive sequence recorded in the cliff-face of Makapu‘u Head (Figure 4A and 4C) (Yamasaki et al., 2011).

Ko‘olau Volcano didn’t always erupt Enriched Loa compositions. Geochemical analyses of older main-stage basalts exposed in the Trans-Ko‘olau tunnel (Jackson et al., 1999) reveal compositions more like Kea-type volcanoes, and main-stage basalts from the submarine Nu‘uanu deposits (Tanaka et al., 2002) and the Ko‘olau Scientific Drilling Project (KSDP) drill-core (Haskins & Garcia, 2004) reveal compositions more like Loa-type volcanoes. It is estimated that the Enriched Loa signature began erupting ~2.6 Ma (Yamasaki et al., 2011) and encompasses only a small volume of the end of the main shield building stage of volcanism (Haskins & Garcia, 2004). This transition from main-shield stage Kea- and Loa-type compositions to late-shield stage Enriched Loa compositions was gradual, becoming more enriched over a timescale of ~2,600-4,600 years based on the whole-rock geochemical change throughout the KSDP drill-core (Haskins and Garcia, 2004). It is possible that injection of an enriched mantle source material would mix with mantle compositions that previously erupted, which explains both the gradual enrichment of the Enriched Loa geochemical signature from the early to late shield stage at Ko‘olau Volcano (Haskins and Garcia, 2004), and the subsequent depletion of the Enriched Loa geochemical signature at Lāna‘i and Kaho‘olawe (Williamson et al., 2025).

1.4 Proposed Project and Overview of Thesis

1.4.1 This Thesis

Within the finer temporal scale of just Ko‘olau-Makapu‘u lavas at Makapu‘u Head and Wheeler Army Airfield drill-core, mixing is evident by cyclic enrichment and depletion of the

Enriched Loa geochemical signature through time (Figure 5). Isotopic compositions will not alter from fractional crystallization, and thus, mixing with another melt composition must occur to result in cycles of isotopic variation. If mixing is occurring in the shallow-crustal magma reservoirs, textural and chemical variety in mineral populations and some mineral-melt reactions may occur. Thus, petrographic analysis of Ko‘olau-Makapu‘u lavas can provide insight into any plumbing system responses to injection of an enriched mantle source magma.

This study aims to build off the previous whole-rock geochemistry and isotopic work from Williamson et al. (2025) through a detailed petrographic, textural, and electron microprobe investigation of olivine, pyroxene, and plagioclase macrocryst, groundmass, inclusion, and reaction-rim phases in the same Ko‘olau-Makapu‘u samples from Wheeler Army Airfield drill-core and Makapu‘u Head, the type-locality and best exposure of Ko‘olau-Makapu‘u lavas.

Multiple questions remain about the Enriched Loa geochemical endmember:

1. Why do Ko‘olau and Lāna‘i Volcanoes lack postshield stages?
2. Are there physical processes that occur in the plumbing system as a result of injection of an isotopically enriched mantle source material that results in the lack of a postshield stage?
3. Are there mineral-melt reactions recorded by the petrography of Ko‘olau-Makapu‘u lavas that indicate mixing between the Enriched Loa geochemical endmember, and earlier erupted Loa-type compositions?

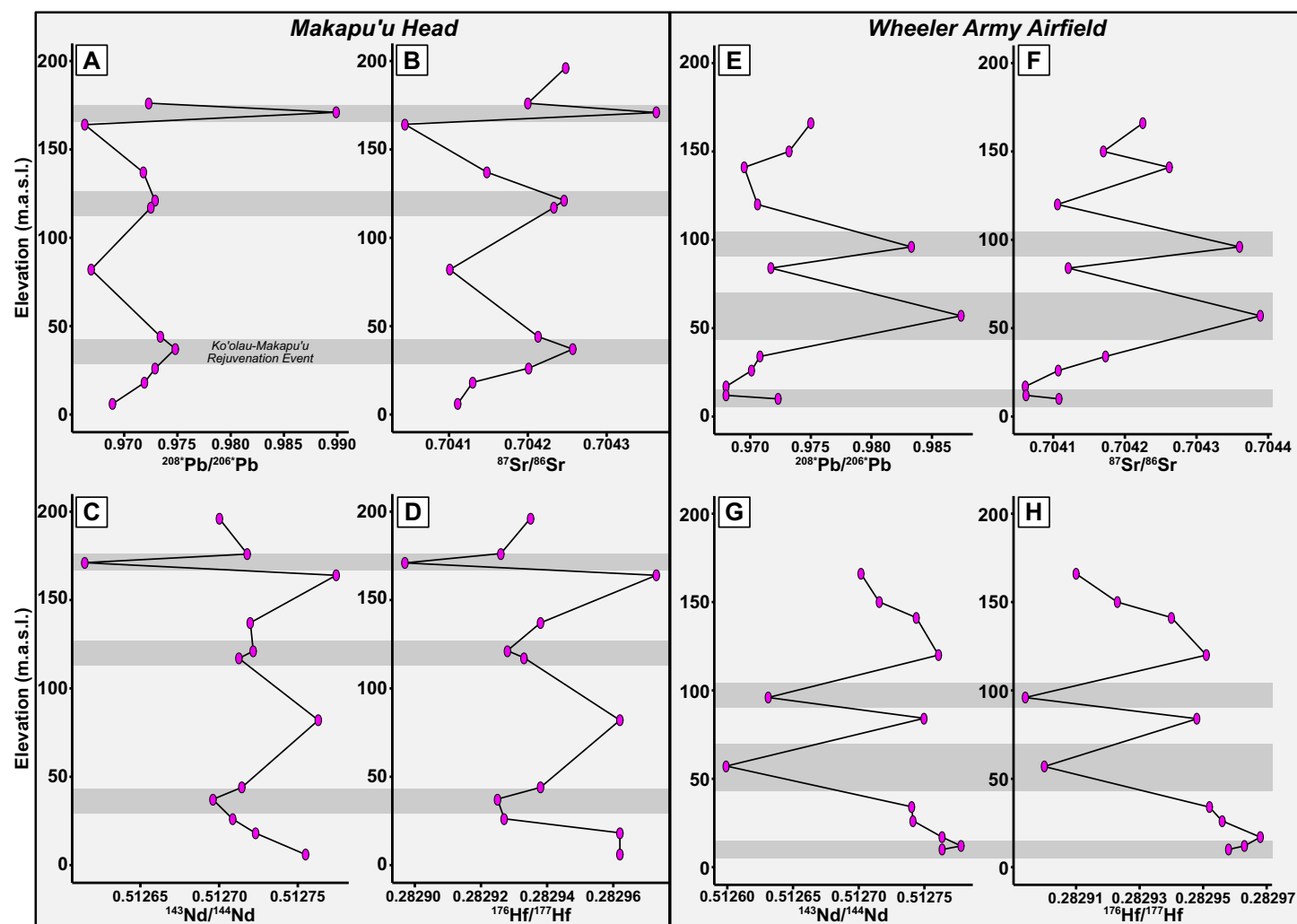


Figure 5: Plots showing whole-rock isotope ratios as a function of stratigraphic order for A) $^{208}\text{Pb}/^{206}\text{Pb}$ at Makapu'u Head, B) $^{87}\text{Sr}/^{86}\text{Sr}$ at Makapu'u Head, C) $^{208}\text{Pb}/^{206}\text{Pb}$ at Wheeler Army Airfield drill-core, D) $^{87}\text{Sr}/^{86}\text{Sr}$ at Wheeler Army Airfield drill-core, E) $^{143}\text{Nd}/^{144}\text{Nd}$ at Makapu 'u Head, F) $^{176}\text{Hf}/^{177}\text{Hf}$ at Makapu 'u Head, G) $^{143}\text{Nd}/^{144}\text{Nd}$ at Wheeler Army Airfield drill-core, and H) $^{176}\text{Hf}/^{177}\text{Hf}$ at Wheeler Army Airfield drill-core. Highlighted sections indicate Ko'olau-Makapu'u rejuvenation events.

Ko‘olau-Makapu‘u samples provide a rare opportunity to study the last volcanic output from Ko‘olau Volcano before it enters an ~1 Ma hiatus of volcanic activity. Ultimately, Ko‘olau-Makapu‘u lavas record the dying of Ko‘olau Volcano, providing insight into the potential petrographic response to an isotopically enriched mantle source derived magma that may lead to premature cessation of volcanic activity. This study provides, for the first time, a petrogenetic model for Ko‘olau-Makapu‘u basalts, documenting the plumbing system response to injection of an enriched mantle source material through a detailed petrographic study of mineral textures, relationships, and multi-phase chemical reactions.

The magmatic plumbing systems for currently erupting Kīlauea Volcano are well constrained from detailed petrography, diffusion chronometry, thermobarometry, and seismic studies (e.g. Anderson et al., 2019; Lin et al., 2014; Neal et al., 2019; P. Wieser et al., 2020a; Wieser et al., 2020b). Similar studies of Mauna Loa reveal a comparable plumbing system to Kīlauea, and thus, Loa- and Kea-type volcanoes may behave similarly although the chemistry of their shield stage basalts is quite different (e.g. Lynn et al., 2024a; Wieser et al., 2025a; Wieser et al., 2025b; Winslow et al., 2025). These types of studies do not currently exist for Ko‘olau Volcano, and thus, our theoretical plumbing system for Ko‘olau, which drives our interpretations and petrogenetic model, mimics those of Kīlauea, with deep (3-5 km depth) and shallow (1-2 km depth) crustal magma reservoirs located below the summit caldera and dikes that variably tap these reservoir(s) and feed magma to the rift zone (Figure 6) (e.g. Weiser et al., 2020b). Ko‘olau began erupting with Loa-type compositions in its early main shield stage and transitions to Ko‘olau-Makapu‘u compositions towards the late shield stage, as evidenced by gradual increase in SiO₂ and decrease in CaO and TiO₂ in the KSDP core (Haskins and Garcia, 2004). Thus, in our plumbing system model for Ko‘olau Volcano, the deep and shallow crustal magma storage

reservoir(s) are established with a cumulate mush of Loa-type compositions, likely dunite with minor amounts of wehrlite and gabbro. The deep reservoir system is rich in high Fo olivine due to the continued replenishment of a primitive, Loa-type melt that keeps the reservoir buffered to high temperature, high MgO compositions that are only fractionating olivine (Rhodes & Hart, 1995). The shallow magma reservoir does not receive sustained replenishment of primitive magma, so it is able to fractionally crystallize to the point of multiple phase saturation and thus contains low Fo olivine, clinopyroxene, and plagioclase. This plumbing system model for Ko‘olau Volcano serves as the basis for our petrologic and mineral chemistry interpretations in this thesis.

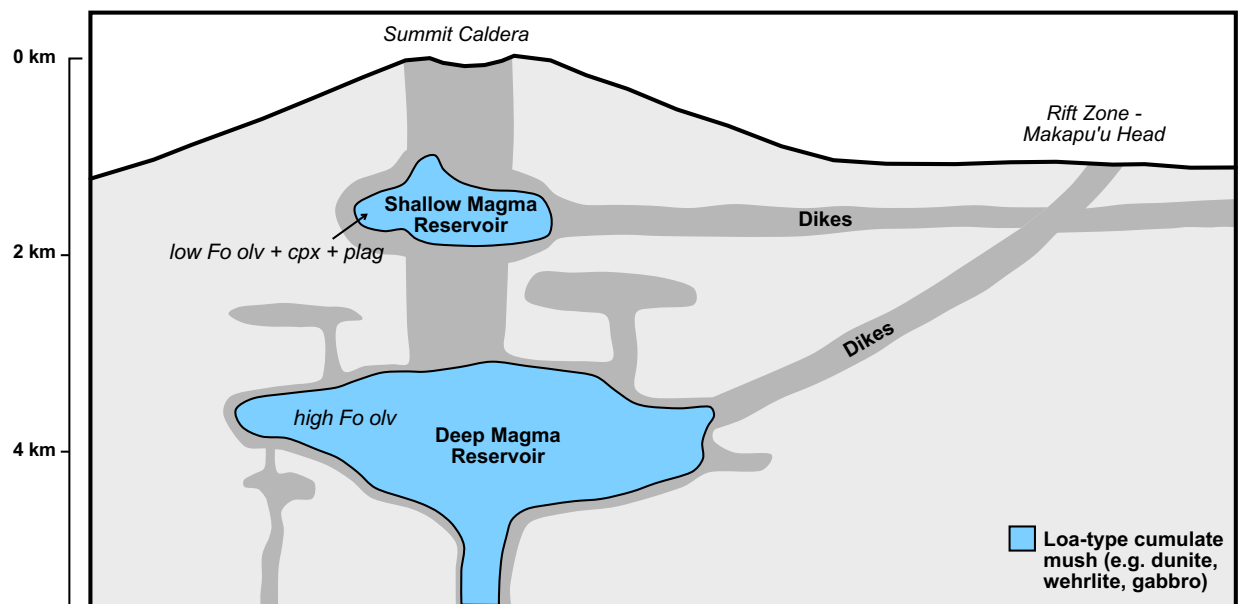


Figure 6: Theoretical plumbing system for Ko'olau Volcano, modified from Kīlauea plumbing system models (Wieser et al., 2020).

1.4.2 Initial Methodology and Deviations

This thesis was originally planned to employ Fe-Mg diffusion chronometry in olivine to quantify magma storage timescales and compare those timescales to currently erupting Kīlauea and Mauna Loa. We aimed to explore the hypothesis that Enriched Loa volcanics bypass

shallow-crustal storage systems, which avoids mixing or dilution with previous magmas produced from higher degrees of melting, and are thus more explosive. Diffusion chronometry studies are mainly employed on tephra of currently erupting volcanoes (e.g. Kīlauea), where alteration is minimal, many samples with plentiful olivine are available, and the rapid quenching of magma preserves the time between the diffusive event (such as magma mixing in the plumbing system or rapid ascent) and eruption (Kahl et al., 2023; Lynn, et al., 2017; Lynn, et al., 2024a; Lynn 2024b). However, multiple challenges prevented successful application of olivine Fe-Mg diffusion chronometry within this sample suite.

One, a sample size of ~20-30 olivine per eruptive event are needed to constrain a reliable diffusion timescale because 1-dimensional diffusion models often have large uncertainties (Shea, et al., 2015a). Our full sample suite encompasses ~0.22 Ma of eruptive history, and each sample represents an individual lava flow, with an unknown amount of time between eruptions. Therefore, it is likely that each lava flow will exhibit different diffusion timescales, and lava flows commonly contain more variety in their diffusion timescales compared to tephra. To constrain a reliable diffusion timescale, ~20-30 olivine per sample (and thus, per lava flow) would need to be analyzed. None of our available samples contain a sufficient amount of olivine to model an accurate and reliable diffusion timescale.

Second, diffusion chronometry on lavas are difficult because lava flows remain hot for more time than tephra as it flows over the Earth's surface after eruption and cools slowly via conduction and convection (Couperthwaite et al., 2022). Continued diffusive re-equilibration of olivine carried in this hot lava flow can make modelled diffusion timescales longer than the time between eruption trigger and eruption, and thus, our timescales may not be comparable to timescales from Kīlauea or Mauna Loa tephra.

Third, olivine in our sample suite have been exposed to meteoric water and surficial weathering processes for 2-3 million years. Upon petrographic investigation of our sample suite, we found that most of the olivine have ~50 μm thick iddingsite alteration rims and exhibit ~100 μm pyroxene overgrowths rims. Iddingsite alteration rims and pyroxene overgrowths likely overprint much of the diffusion timescale recorded by eruption (Couperthwaite et al., 2022). Thus, our diffusion profiles would appear much steeper than they should, and our modelled diffusion timescales would be much shorter than the true diffusion timescale.

With these limitations, Fe-Mg diffusion chronometry of olivine was not a suitable analytical technique for our specific sample suite. However, this study still characterizes the petrography and mineral chemistry of Ko‘olau-Makapu‘u lavas in detail for the first time, resulting in the first petrogenetic model for Ko‘olau-Makapu‘u lavas.

CHAPTER 2 – METHODS

2.1 Samples in this Study

This study investigates 21 late-shield stage Ko‘olau lavas with the Enriched Loa geochemical signature that were previously characterized for high precision trace element concentrations, major element compositions, and Pb-Hf-Nd-Sr isotopic compositions (Armstrong, 2022; Williamson et al., 2025). Fifteen samples were taken from Makapu‘u Head, the type-locality for the Enriched Loa geochemical endmember (Figure 4A and 4C; 14 samples collected February 2015, 1 sample collected September 2024). Six samples are from Wheeler Army Airfield Drill-core located in central O‘ahu (Figure 4A and Figure 7), a water quality monitoring well that recovered a sequence of 29 lava flows from Ko‘olau’s enriched, late-shield stage (Tanaka et al., 2002). Lastly, one sample is included here from the H-3 roadcut (Figure 4A)

Due to their relative distance from the hypothesized caldera and differences in regional dip of the lava flows (Figure 4A), the localities cannot be correlated without further field analyses (Haskins and Garcia, 2004; see Figure 1a and 1b), and thus we treat Makapu‘u Head samples, Wheeler Army Airfield Drill-core samples, and the H-3 dike sample separately, and treat each sample as an individual lava flow. A summary of samples with their reported data is given in Table 1.

2.2 Petrography

Samples were prepared into 30 μm thin sections with a polish suitable for electron microbeam analysis, per standard protocol. Mineral textures and relationships were determined via polarized light microscopy and backscatter electron (BSE) microscopy on a JEOL

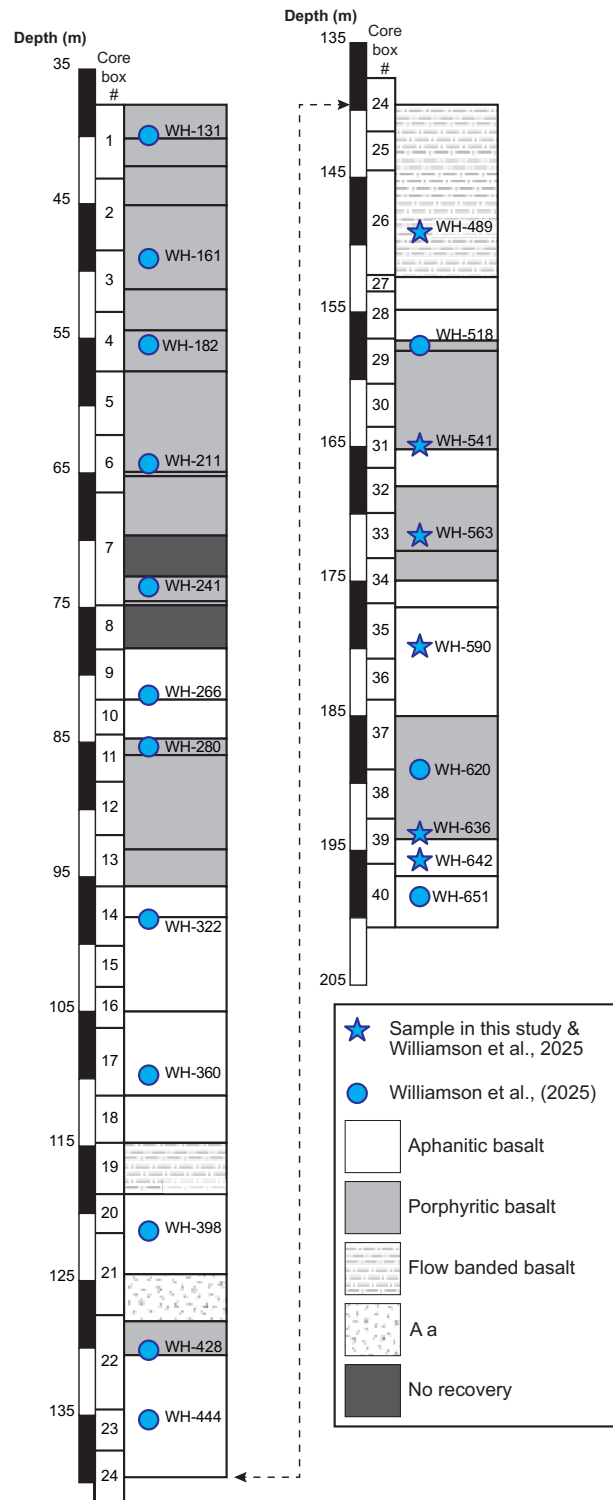


Figure 7: Wheeler Army Airfield drill-core log showing sample locations for Williamson et al. (2025) and this study. Modified from Armstrong (2022).

Table 1: Summary of sample locations and analyses conducted. Whole-rock major and trace elements and radiogenic isotope ratios were conducted by Williamson et al. (2025). In-situ EPMA analyses were conducted in this study. Elevation is in meters above sea level (m.a.s.l.). In EPMA column, Olv = olivine, pyx = pyroxene, plag = plagioclase feldspar, gm = groundmass, and rim = pyroxene reaction rims and pyroxene overgrowths.

				Whole-rock data		Whole-rock radiogenic isotope ratios				
Sample	Latitude	Longitude	Elevation (m.a.s.l.)	Major element oxides	Trace elements	²⁰⁸ Pb/ ²⁰⁶ Pb	¹⁷⁷ Hf/ ¹⁷⁶ Hf	¹⁴⁴ Nd/ ¹⁴³ Nd	⁸⁷ Sr/ ⁸⁶ Sr	EPMA
Makapu'u Head										
KOOb-2	21.3100	-157.6577	5.75	X	X	X	X	X	X	Olv, pyx, gm, rim
MHSep7-4	21.3097	-157.6575	21.59							Olv, pyx, gm, rim
KOOb-4A	21.3098	-157.6575	21.61	X	X	X	X	X	X	Olv, gm
KOOb-5	21.3097	-157.6576	30.67	X	X	X	X	X	X	Olv, pyx, plag, gm, rim
KOOb-6	21.3096	-157.6575	35.15	X	X	X	X	X	X	Olv, gm, rim
KOOb-7	21.3095	-157.6573	40.35	X	X	X	X	X	X	Olv, pyx, gm, rim
KOOb-8	21.3098	-157.6543	122.79	X	X	X	X	X	X	Olv, pyx, gm
KOOb-9B	21.3096	-157.6539	135.91	X	X	X	X	X	X	Olv*, pyx, gm
KOOb-10	21.3095	-157.6538	141.85	X	X	X	X	X	X	Olv, pyx, gm, rim
KOOb-11	21.3094	-157.6533	164.60	X	X	X	X	X	X	Olv

Table 1 cont.

Sample	Latitude	Longitude	Elevation (m.a.s.l.)	Whole-rock data		Whole-rock radiogenic isotope ratios				EPMA
				Major element oxides	Trace elements	$^{208}\text{Pb}/^{206}\text{Pb}$	$^{177}\text{Hf}/^{176}\text{Hf}$	$^{144}\text{Nd}/^{143}\text{Nd}$	$^{87}\text{Sr}/^{86}\text{Sr}$	
KOOB-12B	21.3092	-157.653	183.61	X	X	X	X	X	X	Olv*, pyx, gm
KOOB-13	21.3084	-157.6529	197.04	X	X					
KOOB-14	21.3087	-157.6528	196.79	X	X		X	X	X	Olv
KOOB-15	21.3084	-157.6521	168.07							Olv*,
				X	X	X	X	X	X	pyx, gm, rim
KOOB-16	21.3001	-157.6519	78.85							Olv,
				X	X	X	X	X	X	pyx, gm, rim
<i>Wheeler Army Airfield</i>										
WH-489	21.4542	-158.0330	54.48							Olv,
				X	X	X	X	X	X	pyx, gm, rim
WH-541	21.4542	-158.0330	38.48							Olv*,
				X	X					pyx, gm, rim
WH-563	21.4542	-158.0330	31.48							Pyx, gm, rim
				X	X	X	X	X	X	
WH-590	21.4542	-158.0330	23.48							
				X	X	X	X	X	X	Olv*,
WH-636	21.4542	-158.0330	9.48							pyx, gm
				X	X	X	X	X	X	Olv,
WH-642	21.4542	-158.0330	7.48							pyx, gm
				X	X	X	X	X	X	
<i>Interstate H-3 Roadcut</i>										
H3b-3B	21.4262	-157.7601	32.00							Olv*
				X	X	X	X	X	X	

*Additional EPMA analyses from Armstrong (2022).

JXAiHP200F Field Emission Electron Probe Microanalyzer (EPMA) at Colorado State University.

2.2.1 A Note on Pyroxene Nomenclature

Henceforth in this thesis, orthopyroxene refers to pyroxene with wollastonite (Wo) endmember below 5 mol%, low-Ca clinopyroxene refers to $5 \text{ mol \%} < \text{Wo} < 20 \text{ mol\%}$, and high-Ca clinopyroxene refers to $\text{Wo} > 20 \text{ mol\%}$. Unless specified otherwise, clinopyroxene more generally refers to both low-Ca and high-Ca clinopyroxene. The term pyroxene in this thesis refers to all these endmembers.

2.3 Scanning Electron Microscopy and Phase Mapping

Large area BSE and energy-dispersive spectroscopy (EDS) maps of 10 representative thin sections were completed using a FEI Quanta FEG 450 Field Emission Scanning Electron Microscope (SEM) at the United States Geological Survey Microbeam Laboratory in Denver, Colorado. Analytical conditions were 20 kV, with a 5 μm spot size, a beam intensity of 5, and a working distance of 11 mm. Maps were collected in 10 μm by 10 μm pixels with 256x magnification and a 3% overlap between frames. EDS Maps were collected with a process time of 3 in AZTec software. Following analyses, maps were processed for modal percentages using Weka Trainable Segmentation (WTS), an open-source machine learning plug-in available through the free-access software ImageJ and downloadable through the Fiji package (Arganda-Carreras et al., 2017). Weka is useful for petrographic image processing in geologic contexts, specifically for phase mapping and crystal-size distribution analyses (Lormand et al., 2018; Pettus, 2021). BSE images were processed following the procedure outlined in Lormand et al. (2018). Due to differences in brightness and contrast of BSE images, each thin section was trained separately per phase to bin phases into olivine, pyroxene, plagioclase, vesicle/void, and $\pm$

oxides (Figure 8). Resulting phase percentages were then subtracted from 100% to calculate groundmass percentage. Groundmass mineralogy was determined via electron microprobe and is described further in Chapter 3.

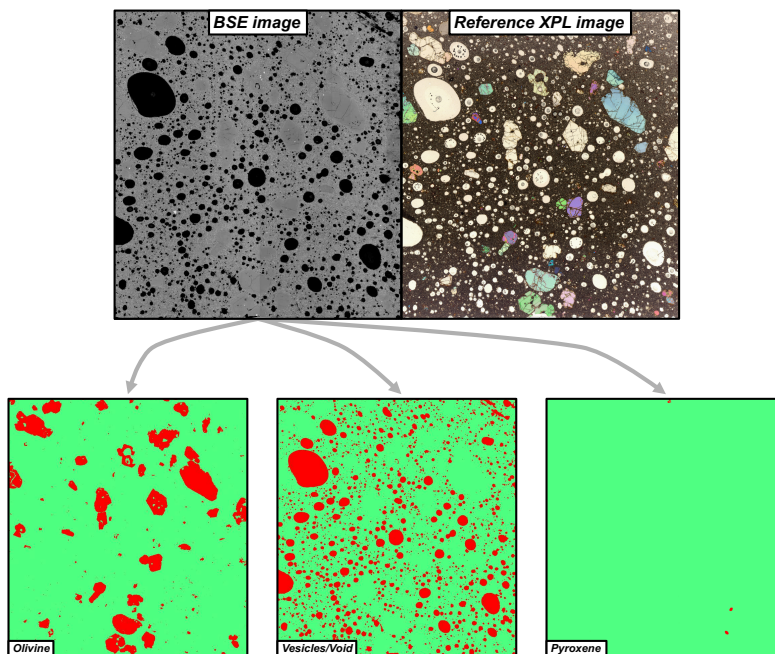


Figure 8: Weka Trainable Segmentation workflow and classified images of each phase for sample WH-636. Red indicates the identified phase and green represents all other un-identified pixels.

2.4 Electron Microprobe Analyses

Mineral chemistry and textural analyses were performed on a JEOL JXAiHP200F Field Emission EPMA at Colorado State University. Macrocryst, groundmass, inclusion, and reaction-rim chemistry were collected on olivine, pyroxene, plagioclase, and spinel phases using point analyses. Core-rim transects were collected on multiple olivine and pyroxene macrocrysts, and high-precision chemical maps were collected on 2 pyroxene phenocrysts and 1 pyroxene rim encasing an olivine macrocryst in sample KOOb-5.

Spot analyses of olivine macrocrysts from samples KOOb-9B, KOOb-12B, KOOb-15, H3b-3B, WH-541, and WH-636 were collected on a JEOL JXA 8500f thermal field EPMA at the

University of Hawai‘i at Mānoa by Catherine Armstrong, a Master’s student at the University of British Columbia (Armstrong, 2022). The data is included here as part of this thesis, as well as additional analyses on these samples conducted in this study.

2.4.1 Analytical Conditions

For analyses collected at University of Hawai‘i at Mānoa, olivine was analyzed at 20 kV and 200 nA with a 10 μm beam size, following the procedure outlined in (Lynn et al., 2017a). Analysis consisted of two or three core points that were averaged for a single core composition and a single rim composition per macrocryst. Si, Mg, Ni, and Ca were analyzed for 100 seconds on-peak, Mn was analyzed for 60 seconds on-peak, and Fe for 30 seconds on-peak.

The remaining analytical conditions described henceforth were collected at Colorado State University as a part of this thesis. Olivine and pyroxene point analyses and core-rim transects were analyzed at 15 - 20 kV and 20 - 50 nA. Electron beam diameter ranged from a focused beam (nominally 0 μm) to 2 μm beam size. Plagioclase point analyses were analyzed at 15 kV and 12 nA with a time dependent intensity (TDI) correction of 2.5 applied to correct for migration of alkali elements under the electron beam. Plagioclase was analyzed using a 2 μm beam size, unless the grain was < 2 μm in size, in which case they were analyzed under a focused beam. Count-times and crystal assignments for each element varied between analyses and are summarized in Appendix A, along with electron beam conditions.

Spinel analyses for olivine-spinel aluminum exchange thermometry (OSAT) were analyzed at 15 kV and 30 nA with a 1 μm beam size. High precision olivine analyses for OSAT were analyzed under a custom method that changed analytical conditions between elements in a two-stage analysis, so that aluminum and chromium could be analyzed with longer count-times and on multiple spectrometers to result in more accurate analyses of these trace elements, which

the thermometer relies upon (see Section 2.5.3). For the first analysis, Mg, Si, Fe, Ni, Mn, and Ca were analyzed at 15 kV and 40 nA with a 5 μm beam size and count-times of 20 or 30 seconds, depending on the element. For the second analysis, Al and Cr were analyzed at 15 kV and 150 nA with a 5 μm beam size and much longer count-times of 60 seconds per element. Count-times and crystal assignments for each condition are summarized in Appendix A. Data for Al and Cr from multiple spectrometers was aggregated in post-processing.

Pyroxene elemental maps were collected at 15 kV and 20 nA with a focused beam, 2x2 μm pixel size, and 500 ms/pixel dwell time. Maps were collected via a two-stage analysis, for which analytical conditions are summarized in Appendix A.

2.4.2 EPMA Precision and Quantifying Error

For olivine analyses collected at University of Hawai'i at Mānoa, two-sigma relative precision based on repeated analyses of San Carlos olivine (USNM 1113120) and Springwater olivine (USNM 2566), respectively, is 0.63 and 0.61 wt.% for SiO_2 , 0.35 and 0.33 wt.% for MgO , 0.06 and 0.06 wt.% for FeO , 0.004 and 0.004 wt.% for MnO , 0.01 wt.% for NiO , and 0.004 wt.% for CaO . The larger of these precision analyses were chosen for each element-oxide to represent the $\pm$ wt.% error for olivine analyses collected at University of Hawai'i at Mānoa.

For olivine analyses collected at Colorado State University, one-sigma sample standard deviation was calculated for each element-oxide based on repeated analyses of geologic reference materials, San Carlos olivine (NMNH 111312-44) and Springwater olivine (USNM 2566). For each element-oxide, the largest standard deviation was chosen among San Carlos or Springwater olivine analyses to represent the $\pm$ wt.% error for unknown EPMA analyses. Olivine analyses display a precision of $\pm 0.26\%$ for SiO_2 , $\pm 0.32\%$ for MgO , $\pm 0.17\%$ for FeO , $\pm 0.01\%$ for MnO , $\pm 0.004\%$ for CaO , ± 0.008 for NiO , and $\pm 0.01\%$ for Cr_2O_3 .

Error was propagated for olivine Forsterite content (Fo mol%) calculations analyzed at Colorado State University and University of Hawai‘i at Mānoa using (1):

$$Fo \text{ Error (mol\%)} = Fo * \sqrt{\left(\frac{\sigma Mg}{Mg}\right)^2 + \left(\frac{\sqrt{\sigma Mg^2 + \sigma Fe^2}}{(Mg + Fe)}\right)^2} \quad (1)$$

Where σMg and σFe represent the $\pm$ mol% error on MgO and FeO analyses, respectively, and Mg and Fe represent the mol% compositions for each analysis.

For pyroxene analyses collected at Colorado State University, one-sigma sample standard deviation was calculated for each element-oxide based on repeated analyses of geologic reference materials, chromium augite (NMNH 164905) and Kakanui augite (NMNH 122142). Similarly, for each element-oxide, the largest standard deviation was chosen among chromium augite or Kakanui augite analyses to represent the $\pm$ error for unknown EPMA analyses. Pyroxene analyses display a precision of $\pm 0.04\%$ for Na₂O, $\pm 0.51\%$ for SiO₂, $\pm 0.09\%$ for Al₂O₃, $\pm 0.13\%$ for MgO, $\pm 0.09\%$ for FeO, $\pm 0.01\%$ for MnO, $\pm 0.09\%$ for CaO, $\pm 0.01\%$ for TiO₂, and $\pm 0.03\%$ for Cr₂O₃.

Error was propagated for Magnesium number (Mg#) calculations using (2):

$$Mg\# \text{ Error (mol\%)} = Mg\# * \sqrt{\left(\frac{\sigma Mg}{Mg}\right)^2 + \left(\frac{\sqrt{\sigma Mg^2 + \sigma Fe^2}}{(Mg + Fe)}\right)^2} \quad (2)$$

Where σMg and σFe represent the $\pm$ mol% error on MgO and FeO analyses, respectively, and Mg and Fe represent the mol% compositions for each analysis.

For plagioclase analyses collected at Colorado State University one-sigma sample standard deviation was calculated for each element-oxide based on repeated analyses of geologic reference material plagioclase (NMNH 115900). Plagioclase analyses display a precision of $\pm 0.18\%$ for Na_2O , $\pm 0.17\%$ for SiO_2 , $\pm 0.19\%$ for Al_2O_3 , $\pm 0.01\%$ for MgO , $\pm 0.08\%$ for FeO , $\pm 0.02\%$ for MnO , $\pm 0.12\%$ for CaO , $+0.01\%$ for TiO_2 , and $\pm 0.01\%$ for K_2O .

Error was propagated for Anorthite number (An#) calculations using (3):

$$\begin{aligned} & \text{An\# Error (mol\%)} \\ &= \sqrt{\left(\frac{\sigma \text{Ca}}{\text{Ca}}\right)^2 + \left(\frac{\sqrt{\sigma \text{Ca}^2 + \sigma \text{Na}^2 + \sigma \text{K}^2}}{\text{Ca} + \text{Na} + \text{K}}\right)^2} \end{aligned} \quad (3)$$

Where σCa , σNa , and σK represent the $\pm$ mol% error on CaO , Na_2O , and K_2O analyses, respectively, and Ca , Na , and K represent the mol% compositions for each analysis. Error propagation was also calculated for Albite (Ab#) and Orthoclase (Or#) mineral endmembers as follows, using (4) and (5) respectively:

$$\begin{aligned} & \text{Ab\# Error (mol\%)} \\ &= \sqrt{\left(\frac{\sigma \text{Na}}{\text{Na}}\right)^2 + \left(\frac{\sqrt{\sigma \text{Ca}^2 + \sigma \text{Na}^2 + \sigma \text{K}^2}}{\text{Ca} + \text{Na} + \text{K}}\right)^2} \end{aligned} \quad (4)$$

$$\begin{aligned} & \text{Or\# Error (mol\%)} \\ &= \sqrt{\left(\frac{\sigma \text{K}}{\text{K}}\right)^2 + \left(\frac{\sqrt{\sigma \text{Ca}^2 + \sigma \text{Na}^2 + \sigma \text{K}^2}}{\text{Ca} + \text{Na} + \text{K}}\right)^2} \end{aligned} \quad (5)$$

For spinel analyses collected at Colorado State University one-sigma sample standard deviation was calculated for each element-oxide based on repeated analyses of geologic

reference material chromite (NMNH 117075). Chromium spinel analyses display a precision of $\pm 0.25\%$ for Al_2O_3 , $\pm 0.07\%$ for MgO , $\pm 0.15\%$ for FeO , $\pm 0.01\%$ for MnO , and $\pm 0.38\%$ for Cr_2O_3 .

Data collected at Colorado State University and University of Hawai‘i at Mānoa on the same samples were compared to test for reproducibility of data between laboratories and electron microprobes. Analyses of the same olivine grains show that both laboratories produce data that are within error for major and trace elements (Figure 9). Thus, we can say that the data produced by Colorado State University is of comparable quality to the data produced by the University of Hawai‘i at Mānoa.

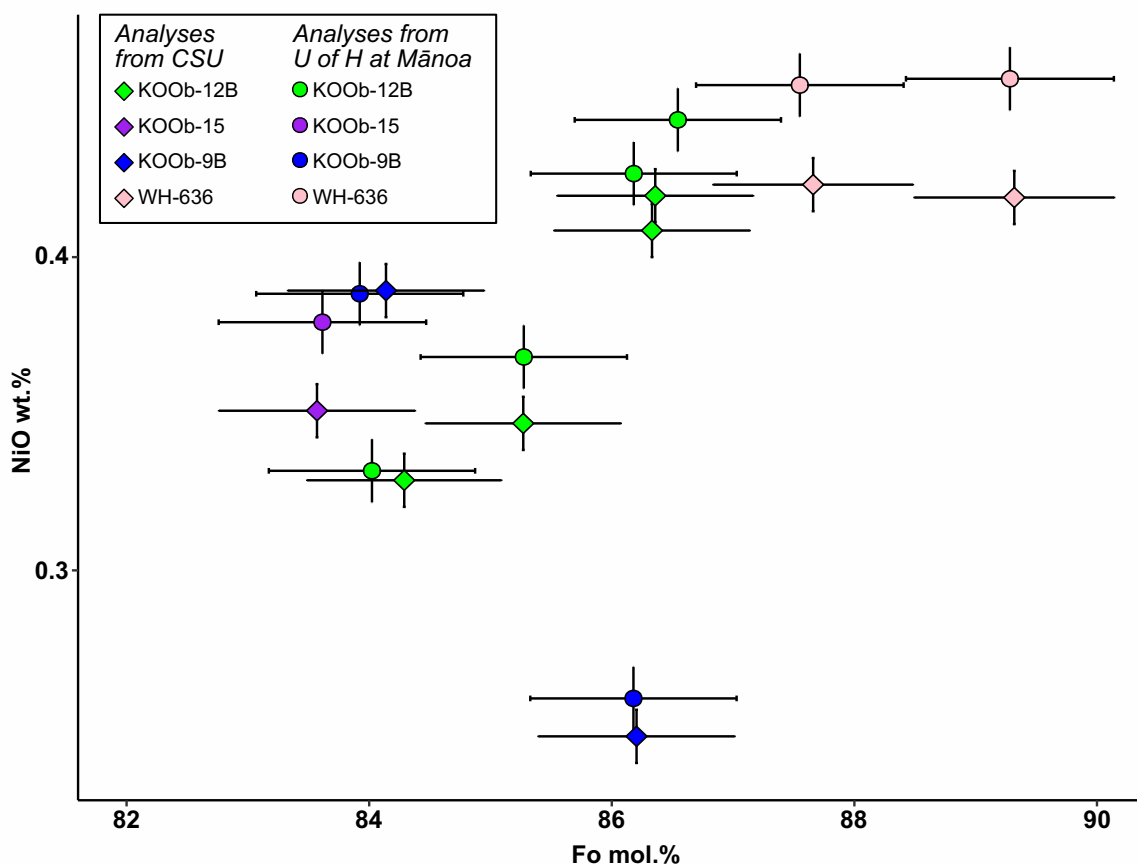


Figure 9: Fo wt.% versus NiO wt.% for the same olivine grains analyzed at different laboratories (denoted by shape). Horizontal and vertical error bars represent $\pm$ error of Fo mol% and NiO wt.%, respectively, reported in Supplementary Information A, Table 1.

2.4.3 EPMA Accuracy

To test instrument accuracy and reproducibility for analyses collected at Colorado State University, at least 3 points of Smithsonian standards were analyzed under the same conditions as unknown points every ~2 hours of analyses. We aim for 5% variance or better for major elements (element concentrations > 5 wt.%), 10% variance or better for minor elements (element concentrations 1-5%), and 30% variance or better for trace elements (element concentrations < 1%). Relative standard deviations (RSD) were used to assess if high percent variances were due to poor analyses (RSD > 10%) or compositional variability (RSD < 10%) within these natural reference materials. Standards, with their variance per element analyzed, is summarized in Table 2. It is commonly known that natural samples contain chemical variability within them. We aim to point out those natural variabilities here to explain the accuracy of the data collected. The full suite of data collected on repeated standard analyses are reported in Supplementary Information B.

Table 2: Maximum percent variance for major, minor, and trace elements between analyzed element-oxides and published compositions for Smithsonian standards used as monitors for EPMA analyses.

<i>Monitor</i>	<i>Maximum variance (%)</i>		
	<i>Majors</i>	<i>Minors</i>	<i>Traces</i>
<i>San Carlos Olivine</i>	1.70	/	13.42*
<i>Springwater Olivine</i>	1.92	/	29.94
<i>Chrome-Augite</i>	1.50*	2.13	16.36
<i>Kakanui Augite</i>	3.96	*	13.87
<i>Chromite</i>	3.61	/	14.43
<i>Plagioclase</i>	1.66	2.73	24.08*

*Percent variances with known natural variability; see explanation below.

For olivine analyses, San Carlos olivine (NMNH 111312-44) and Springwater olivine (USNM 2566) were used as monitors and standards. San Carlos olivine displays a 1.70% variance or better from published compositions for major elements, and 84.92% variance or better for trace elements. The 84.92% variance for trace elements can be explained by the large difference between measured CaO wt.% and published CaO wt.%, however, we consistently measure higher CaO wt.% compared to published compositions, with a maximum RSD of 5.36% for measured data. Thus, this high variance can be explained by naturally variability between standards. Not accounting for the natural variability of CaO wt.% in San Carlos olivine, there is a 13.42% variance or better for trace element compositions. Springwater olivine displays a 1.92% variance or better for major elements and a 29.94% variance or better for trace elements.

For pyroxene analyses, chromium augite (NMNH 164905) and Kakanui augite (NMNH 122142) were used as standards and monitors. Chromium augite displays a 6.25% variance or better for major elements, 2.13% variance or better for minor elements, and a 16.36% variance or better for trace elements. The 6.25% variance or better can be explained by a natural variability of Al₂O₃ wt.%, which displays a 1.70% RSD. Not accounting for this, major elements display a 1.50% variance or better for major elements. Kakanui augite displays a 3.95% variance or better for major elements, 11.43% variance or better for minor elements, and 13.87% variance or better for trace elements. The high percent variance for minor elements can be explained by the variable Na₂O wt.% analyses, which displays a 2.56% RSD. Not accounting for this, pyroxene analyses display an overall 3.95% variance for major elements, 2.13% variance for minor elements, and 16.36% variance for trace elements.

For Cr-spinel analyses, chromite (NMNH 117075) was used as a standard and monitor, displaying 3.61% variance or better for major elements and 14.43% variance or better for trace elements.

Finally, for plagioclase analyses, plagioclase (NMNH 115900) was used as a standard and monitor, displaying 1.66% variance or better for major elements and 2.73% variance or better for minor elements. Trace elements MnO and K₂O both display high percent variance of 59.31% and 38.57%, respectively, with high RSDs of 540.71% and 11.73%, respectively. Because of the high RSDs, this is interpreted as poor analyses for these trace element concentrations, and thus, MnO and K₂O will not be considered for interpretations of plagioclase trace element compositions. Not accounting for these effects, plagioclase displays a 24.08% variance or better for trace elements.

2.4.4 Treatment of Data

Any data with total wt.% < 98% or total wt.% > 102% were removed from consideration assuming they were poor analyses, for example from beam volume contamination with fractures, underlying groundmass, or in the case of olivine, iddingsite weathering rims. Furthermore, outliers in chemical plots with adequate total wt.% were assessed for collection too close to grain edges that therefore may likely contain signals from other phases. Mineral end-member compositions were calculated for olivine, pyroxene, and plagioclase analyses based on mol.% of major elements. All EPMA data collected with their calculated precisions and mineral end-member calculations are reported in Supplementary Information A, Tables 1 - 5.

2.4.5 Comparison Electron Microprobe Data

Geochemical data from other studies were obtained from the GeoRoc (Geochemistry of Rocks of the Oceans and Continents) database (<https://georoc.eu/georoc/new-start.asp>) on

February 25, 2026. We include data for olivine, pyroxene, orthopyroxene, clinopyroxene, plagioclase, feldspar, anorthoclase, spinel, chromite, and chrome-spinel for all Hawaiian volcanoes to expand our Ko‘olau dataset and provide comparison to other Kea, Loa, and Enriched Loa volcanoes. To be comparable to the data in this study, only mineral chemistry data is considered from shield-stage volcanic rocks (tholeiitic basalts, basalts, or picrites) collected via electron microprobe after the year 2000. Only lavas with a complete set of major element compositions for each phase were considered (e.g. SiO₂, iron reported as some combination of FeO, FeO_T, or Fe₂O₃, and MgO for olivine analyses). GeoRoc data is processed the same as the data in this study, with wt. % totals < 98 or wt. % totals > 102 being removed. Additional published Ko‘olau data was included from Ireland et al. (2009), Sakyi et al. (2012), Sobolev et al. (2007), and Weinstein et al. (2004). All literature and GeoRoc data included in this study are reported in Supplementary Information A, Tables 6 and 7.

2.4.6 Compositional Statistics of EPMA Data

NiO wt.%, MnO wt.%, and CaO wt.% have been described as systematically different in Ko‘olau-Makapu‘u basalts when compared to other Hawaiian lavas (Sobolev et al., 2005, 2007). To test differences in these trace element compositions, a non-parametric Mann-Whitney U test was used to compare Ko‘olau-Makapu‘u data with other Hawaiian volcanoes, on the basis that trace element compositions for Ko‘olau-Makapu‘u data are non-normally distributed (Figure 10) and continuous. For Ko‘olau Makapu‘u data, we use data collected in this study (Supplementary Information A, Table 2) as well as outputs from GeoRoc database and data from Sobolev et al. (2007) (Supplementary Information A, Table 7). For other Hawaiian volcanoes, we use data from GeoRoc database (Supplementary Information A, Table 6). All data used for statistical analysis represent the cores of olivine macrocrysts.

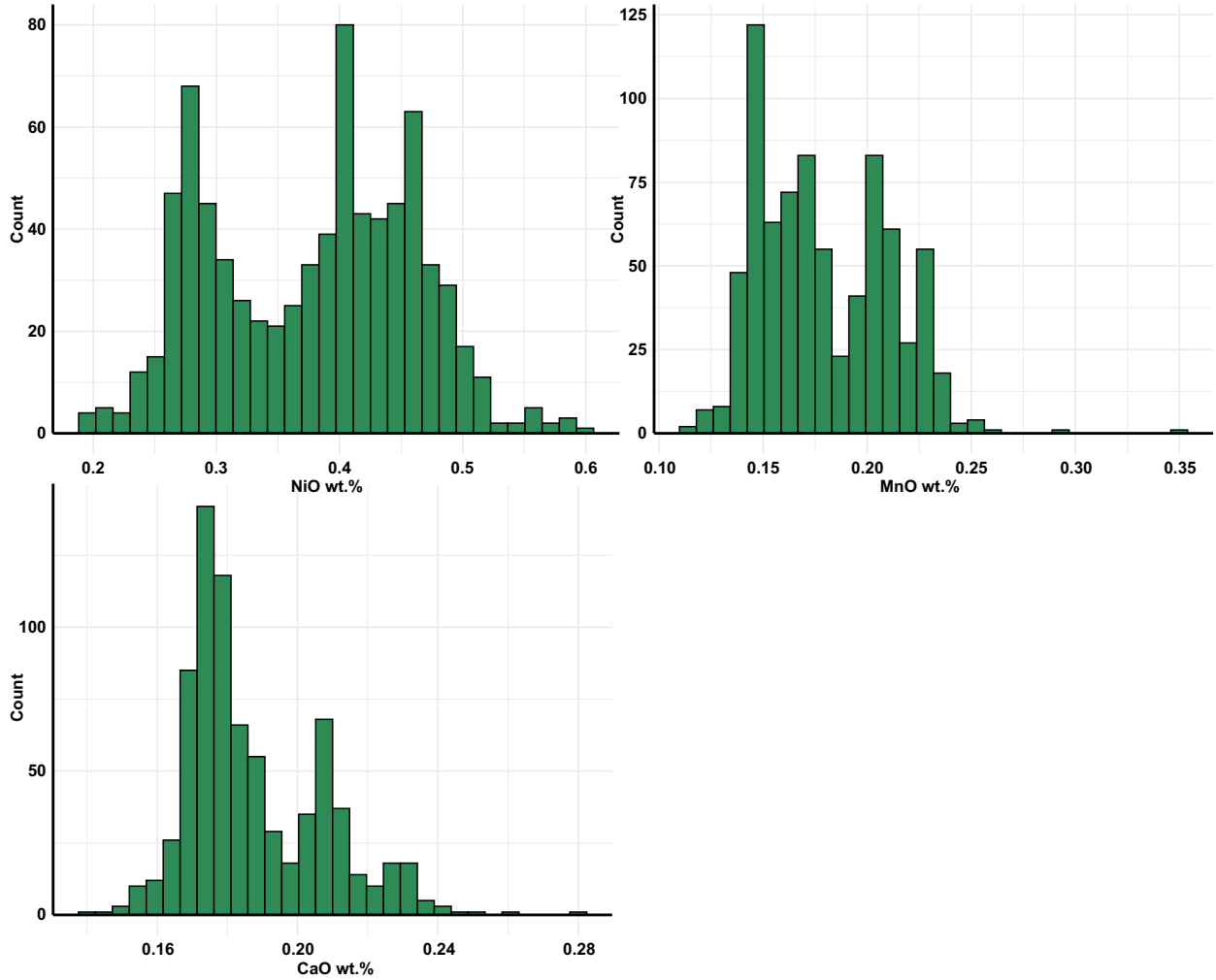


Figure 10: Histograms of NiO wt.%, MnO wt.%, and CaO wt.% olivine core concentrations from Ko‘olau-Makapu‘u lavas used for Mann-Whitney U test (both literature data and data analyzed in this study). Data is non-normally distributed, which justifies the use of the Mann-Whitney U test.

The Mann-Whitney U test was used to analyze the difference in NiO wt.%, MnO wt.%, and CaO wt.% for the two datasets, for which the null hypothesis (H_0) is that the two populations are equal, and the alternative hypothesis (H_1) is that the two populations are not equal. We tested Ko‘olau vs. other Hawaiian volcanoes’ trace element compositions in three runs: Run #1 tested published Ko‘olau-Makapu‘u data and measured data in this thesis against published data from other Hawaiian volcanoes (e.g. Kīlauea, Mauna Loa, Mauna Kea, Haleakalā, Hualālai, Wai‘anae, and Kaua‘i), Run #2 tested only measured trace element compositions in this thesis against

published data from other Hawaiian volcanos, and Run #3 tested measured Ko‘olau-Makapu‘u data in this thesis against published Ko‘olau-Makapu‘u data. This was done to assess the variety in strength of a difference in values and potential biases within olivine datasets.

A significance level of $p\text{-value} < 0.05$ was used to test for statistical significance. For statistically significant values, an r -value was calculated to assess the degree of significance, for which, an $r\text{-value} < 0.3$ denotes a small significance, $0.3 < r\text{-value} < 0.5$ denotes a moderate significance, and $r\text{-value} > 0.5$ denotes a large significance.

2.5 Thermometry Calculations

2.5.1 Tests for Equilibrium

Thermometry is a valuable tool that can model the crystallization temperature of various phases based on thermodynamically-based and experimentally-derived relationships between mineral and melt equilibrium, which can provide constraints on heat input into a volcanic system and relative crystallization histories of multiple phenocryst populations (Putirka, 2008; Wieser et al., 2025a). To employ thermometry, the mineral phases in question must be in equilibrium with their comparative mineral phase or liquid composition used to model temperatures, and thus, it is necessary to employ various equilibrium tests (Putirka, 2008; Wieser et al., 2025a). A Rhodes Diagram is commonly used to assess mineral-melt equilibrium pairs; minerals within the equilibrium field on Rhodes Diagrams are considered in equilibrium with whole-rock compositions, and are good candidates for thermometry calculations (Dungan & Rhodes, 1978; Putirka, 2008; Rhodes et al., 1979). Rhodes Diagrams were plotted for olivine, orthopyroxene, and clinopyroxene using whole-rock compositions from Williamson et al. (2025) for liquid compositions due to the lack of glass in the sample suite. For olivine, $K_d = 0.3 \pm 0.03$ was used (Roeder & Emslie, 1970), and olivine macrocrysts were tested with their respective host whole-

rock compositions. Similarly, orthopyroxene phenocrysts and groundmass phases were tested the same way, with $K_d = 0.29 \pm 0.06$ (Putirka, 2008). The few clinopyroxene antecrysts and groundmass grains, were similarly tested, using a $K_d = 0.27 \pm 0.03$ (Putirka, 2008).

Thermobar is an open-source Python3 package developed to calculate pressures, temperatures, and evaluate melt-mineral equilibria based on various techniques (Wieser et al., 2022). *Thermobar* melt matching is a tool that can automate this process, and report mineral-melt equilibrium pairs efficiently. For establishing mineral-melt equilibrium pairs, *Thermobar* melt matching was used, using the distribution coefficients outlined above.

2.5.2 Orthopyroxene – Liquid Thermometry

Orthopyroxene macrocrysts, groundmass phases, and reaction-rim grains that were found to be in equilibrium with their whole-rock compositions were analyzed for temperature using *Thermobar*, which uses Equation 28a from Putirka (2008) with a fixed pressure and water content, here shown as (6):

$$\begin{aligned} \frac{10^4}{T(^{\circ}C)} = & 4.07 - 0.329[P(GPa)] + 0.12[H_2O^{liq}] \\ & + 0.567 \ln \left[\frac{X_{Fm_2Si_2O_6}^{opx}}{(X_{SiO_2}^{liq})^2 (X_{FeO}^{liq} + X_{MnO}^{liq} + X_{MgO}^{liq})^2} \right] \\ & - 3.06[X_{MgO}^{liq}] - 6.17[X_{KO_{0.5}}^{liq}] + 1.89[Mg\#^{liq}] + 2.57[X_{Fe}^{opx}] \end{aligned} \quad (6)$$

Where $P(GPa)$ = pressure in GPa, H_2O^{liq} = water content of the melt, X_{Fe}^{opx} = the number of Fe cations in opx calculated on a 6 oxygen basis, $Mg\#^{liq}$ = the calculated Mg# of the melt (in this case, whole-rock chemistry), and X_i^j = the mole fraction of i in phase j , for which within term i , $Fm_2Si_2O_6$ = the mole fraction of enstatite and ferrosilite, or, Fe + Mn + Mg and $KO_{0.5}$ = cation fraction of K in the melt calculated on a 0.5 oxygen basis.

Pressure and water content was not determined for this study, and a lack of data exists for these measurements on Ko‘olau lavas. Thus, for water content, we use 0.40 wt.%, an estimated primary H₂O content for Ko‘olau Volcano from olivine-hosted melt inclusions (Hauri, 2002). This is similar to estimated primary water contents for other Hawaiian volcanoes (e.g. Kama‘euakanaloha, Kīlauea, Mauna Loa, Mauna Kea) (Hauri, 2002; Moore, 1970; Wallace, 1998). Nonetheless, Equation 28a is not sensitive to water content. Keeping the pressure constant at 45 MPa (see below) and altering the H₂O content from 0.04% to 0.84% to account for the entire variability of measured H₂O content from Ko‘olau volcano (Hauri, 2002) only changes calculated temperatures by an average of 13.96°C, which is within the established $\pm 41^\circ\text{C}$ error for the thermometer (Putirka, 2008).

For pressure we use 45 MPa, which is similar to estimated pressures of shield stage magma storage conditions from other Hawaiian volcanoes (e.g. Kīlauea, Mauna Loa, Haleakalā) (DeVitre et al., 2024; Gazel et al., 2025; Lynn et al., 2017a; Lynn et al., 2024b) and within the range of calculated pressures for orthopyroxene phenocrysts in Mauna Loa (Winslow et al., 2025). Equation 28a is even less sensitive to variations in pressures. Keeping water content constant at 0.40% (see above) and altering pressure from 44 MPa to 77 MPa (Winslow et al., 2025) only alters calculated temperatures by an average of 1.58°C, which is within the established error of $\pm 41^\circ\text{C}$ for the thermometer (Putirka, 2008).

2.5.3 Olivine-Spinel Aluminum Exchange Thermometry (OSAT)

Olivine macrocryst crystallization temperatures were determined through Olivine-Spinel Aluminum Exchange Thermometry (OSAT) (Coogan et al., 2014; Wan et al., 2008; Zhang et al., 2023) using Equation 8 from Zhang et al. (2023), here shown as (7):

$$T(K) = \frac{10,000}{0.049(0.241) - 0.657(0.040) \ln K_{DAI} - 0.389(0.041) \ln K_{DCr} + 0.543(0.121)Cr\#} \quad (7)$$

Where K_{DAI} is the partition coefficient of aluminum between olivine and spinel in weight percent ($Al_2O_3^{Olv}/Al_2O_3^{Spn}$), K_{DCr} is the partition coefficient of chromium between olivine and spinel in weight percent ($Cr_2O_3^{Olv}/Cr_2O_3^{Spn}$), and $Cr\#$ is the molar ratio of chrome-spinel ($Cr/Cr+Al$). This equation incorporates the coupled substitution of chromium and aluminum in the olivine crystal structures (Zhang et al., 2023) and was chosen because Ko‘olau olivine has high-Cr and therefore likely an Fe-Mg re-equilibration effect, for which the empirical models best represent (Zhang et al., 2023).

In EPMA analyses, primary X-rays are known to penetrate much deeper into the sample substrate, thus exciting surrounding atoms and creating secondary X-rays which may be produced from mineral phases that are not the target analyte (Borisova et al., 2018; Llovet et al., 2012). Chromium is known to suffer this secondary fluorescence effect, in which Cr ions in spinel become excited during olivine analyses and emit X-rays, which results in an overestimation of the olivine Cr content (Llovet et al., 2020). This can affect temperature calculations using this equation, which relies on accurate measurements of Cr concentration in olivine. We used PENFLUOR/FANAL, a Monte Carlo simulation tool within Probe for EPMA (PFE), to model and correct for the effect of secondary fluorescence (Donovan et al., 2019; Donovan & Moy, 2025; Llovet et al., 2012). PENFLUOR/FANAL takes representative olivine and chrome-spinel compositions from our samples to model the observed wt.% Cr in olivine at a given distance from chrome-spinel inclusions, considering the effect of fluorescence.

The effect of fluorescence on olivine compositions for various distances from the spinel inclusion, represented as a percent, was calculated from PENFLUOR/FANAL modelling output using (8):

$$Fluorescence\ Effect\ (\%) = \left| \frac{Observed\ Cr^{olv} - Primary\ Cr^{olv}}{Observed\ Cr^{olv}} * 100 \right| \quad (8)$$

Where Observed Cr^{olv} is the modelled Cr content in the olivine in wt.% with the effect of fluorescence at a given distance from chrome-spinel inclusions and Primary Cr^{olv} is the modelled Cr content in the olivine in wt.% without the effect of fluorescence at a given distance from chrome-spinel inclusions. The effect of fluorescence is shown visually in Figure 11. Each measured olivine chromium composition was then corrected using (9):

$$Corrected\ Cr^{olv} = Measured\ Cr^{olv} * \frac{100 - y}{100} \quad (9)$$

Where y represents the polynomial regression equation (10), fit to the Distance vs. Fluorescence Effect (%) line (Figure 11):

$$y = 0.0058x^2 - 1.3987x + 92.781 \quad (10)$$

Where x represents the distance in microns between measured olivine EPMA points and the spinel inclusion. This distance was measured using secondary electron images (SED) and ImageJ image processing software.

Spinel compositions were recalculated considering iron speciation (Fe^{3+} and Fe^{2+}). After olivine and spinel compositions were re-calculated, the pairs with olivine total wt. % < 98% and/or spinel total wt. % < 97% were considered poor analyses and removed. Temperatures were then

calculated using the supplementary Excel table from Zhang et al. (2023), which applies a $\pm 34.2^\circ\text{C}$ error on calculated temperatures.

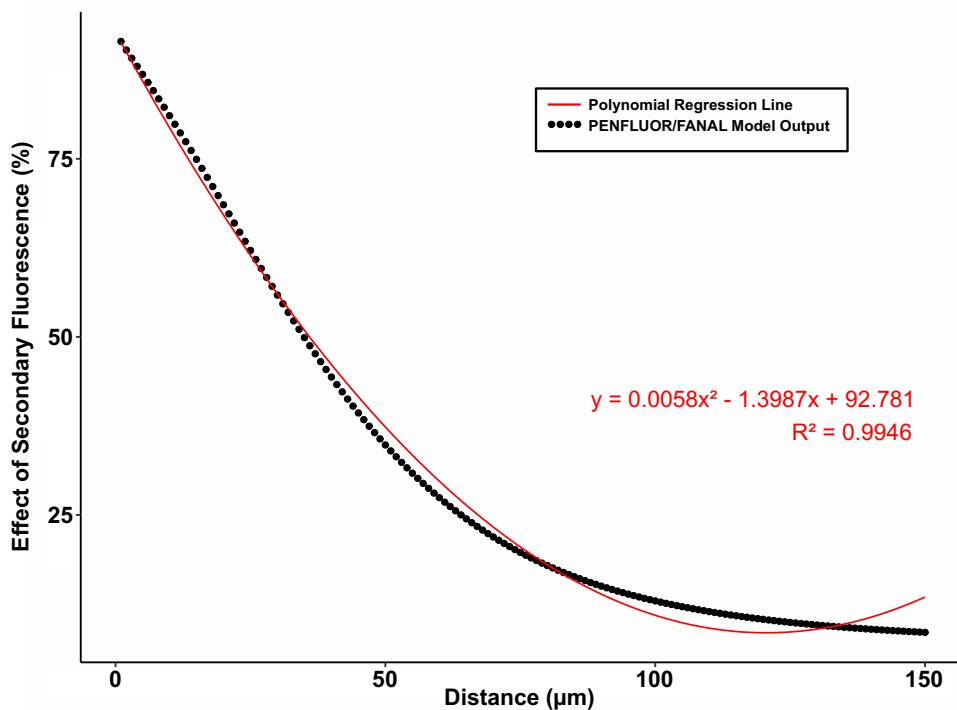


Figure 11: Model output from PENFLUOR/FANAL displaying percent contribution of Cr content from secondary fluorescence as a function of distance from the spinel inclusion with a polynomial regression line.

2.5.4 A Note on Thermometry Error

For both orthopyroxene-liquid thermometry and OSAT, we accept the published error associated with each thermometer; $\pm 41^\circ\text{C}$ for orthopyroxene-liquid (Putirka, 2008) and $\pm 34.2^\circ\text{C}$ for OSAT (Zhang et al., 2023). It is possible to propagate error from EPMA analyses through the thermometry calculations. However, the largest uncertainty in thermobarometry calculations is derived from the experimental studies used to calibrate the equations, not within the EPMA analyses used as input for thermometry calculations. The published uncertainty associated with each thermometer is the uncertainty associated with the calibrations for each thermometer, and thus best represent the uncertainty for each calculation.

CHAPTER 3 – RESULTS

3.1 Petrography

3.1.1 Groundmass

Groundmass crystals contain a large variety in sizes, ranging from 20 – 700 μm within the entire sample suite (Figure 12A and 12B). Groundmass is ubiquitously equigranular within individual samples, although the average size of groundmass crystals varies per samples. Nonetheless, groundmass crystals are discernably smaller than the associated macrocryst phases, which range in sizes up to 2000 μm or greater. Thus, groundmass is here defined as the matrix of equigranular crystals and glass surrounding the relatively larger macrocrysts.

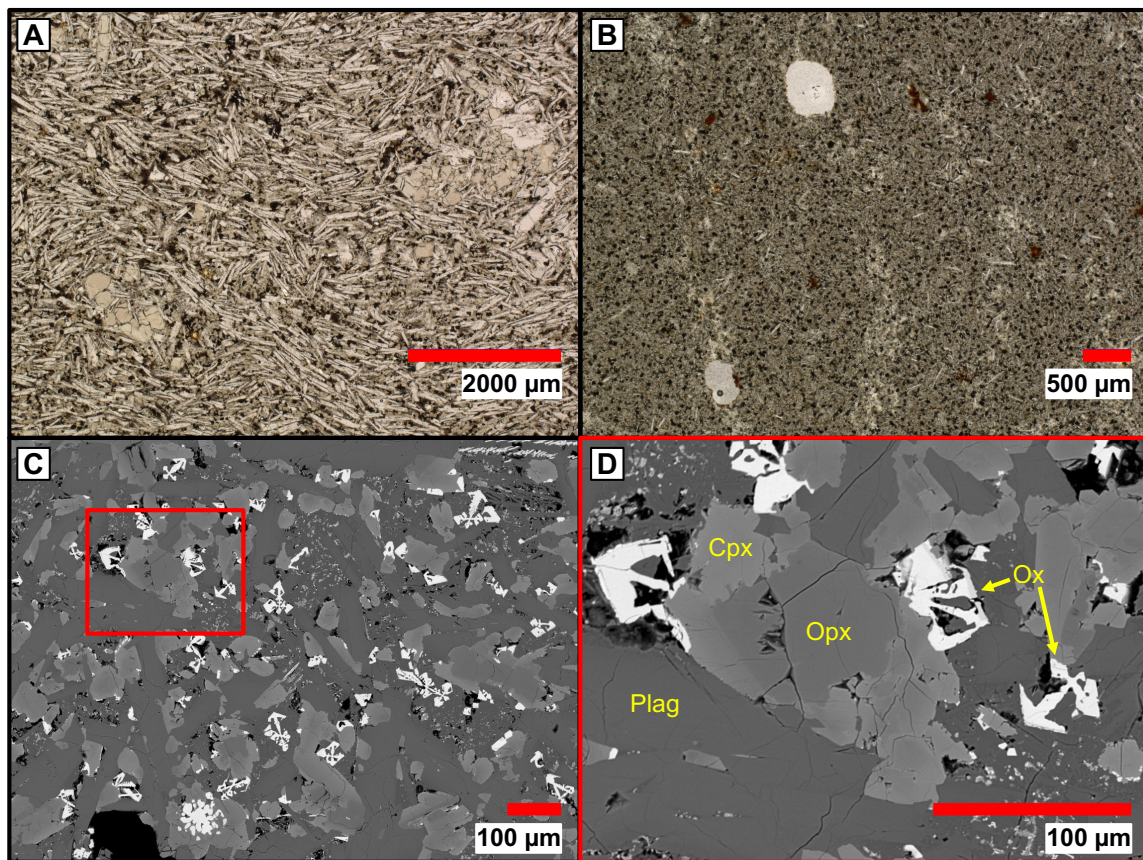


Figure 12: A) Photomicrograph in plane polarized light showing a sample with the most crystallized groundmass; sample is medium grained and intergranular. B) Photomicrograph in

plane polarized light showing the finest grained groundmass crystallinity. C) Representative BSE image of groundmass. Red box is the area depicted in panel D. D) BSE image of groundmass phases: Plag = plagioclase feldspar, Cpx = clinopyroxene, Opx = orthopyroxene, Ox = oxide.

Ko‘olau-Makapu‘u lava samples are porphyritic and hypocrySTALLINE with rare glass amid largely crystalline plagioclase, clinopyroxene, orthopyroxene, and oxides, $\pm$ olivine. Groundmass plagioclase commonly forms well-developed laths that range in length from 20 to 600 μm (Figure 13A). Groundmass clinopyroxenes and orthopyroxenes are less well-developed and commonly form a range of anhedral-subhedral crystals as well as elongated laths, ranging in length from 20 to 700 μm . Like pyroxene phenocrysts, groundmass pyroxene can be zoned from an orthopyroxene core to clinopyroxene rim (Figure 13; Figure 12C and 12D), although, groundmass pyroxenes are dominantly high-Ca clinopyroxenes (Figure 13). Groundmass oxides range in morphologies from euhedral, diamond-shaped crystals to skeletal or dendritic morphologies, typically $< 100 \mu\text{m}$ in size (Figure 12C and 12D). Notably, olivine only occurs in the groundmass of 4 samples: KOOB-12b, WH-636, WH-541, and WH-590. These samples are dominantly in the bottom of the Wheeler Army Airfield drill-core (9.48 – 38.48 m.a.s.l.), with one sample (KOOB-12B) near the top of the Makapu‘u Head stratigraphic column (183.61 m.a.s.l.). It cannot be said whether Makapu‘u Head sample KOOB-12B is temporally correlated to Wheeler Army Airfield samples WH-636, WH-541, or WH-590. Furthermore, samples above ~ 55 m.a.s.l. in the Wheeler Army Airfield drill-core were not analyzed in this study and no detailed petrographic description of the core exists to establish the presence or absence of olivine in the groundmass of these samples. Thus, no trend can be discerned regarding olivine in the groundmass of the Makapu‘u Head and Wheeler Army Airfield sample suite, and no trend is evident when comparing the isotopic signature of samples with olivine in the groundmass (Figure 5). Where olivine occurs in the groundmass, however, they are subhedral-euhedral crystals ranging in size from 20 to 200 μm and are completely altered to iddingsite.

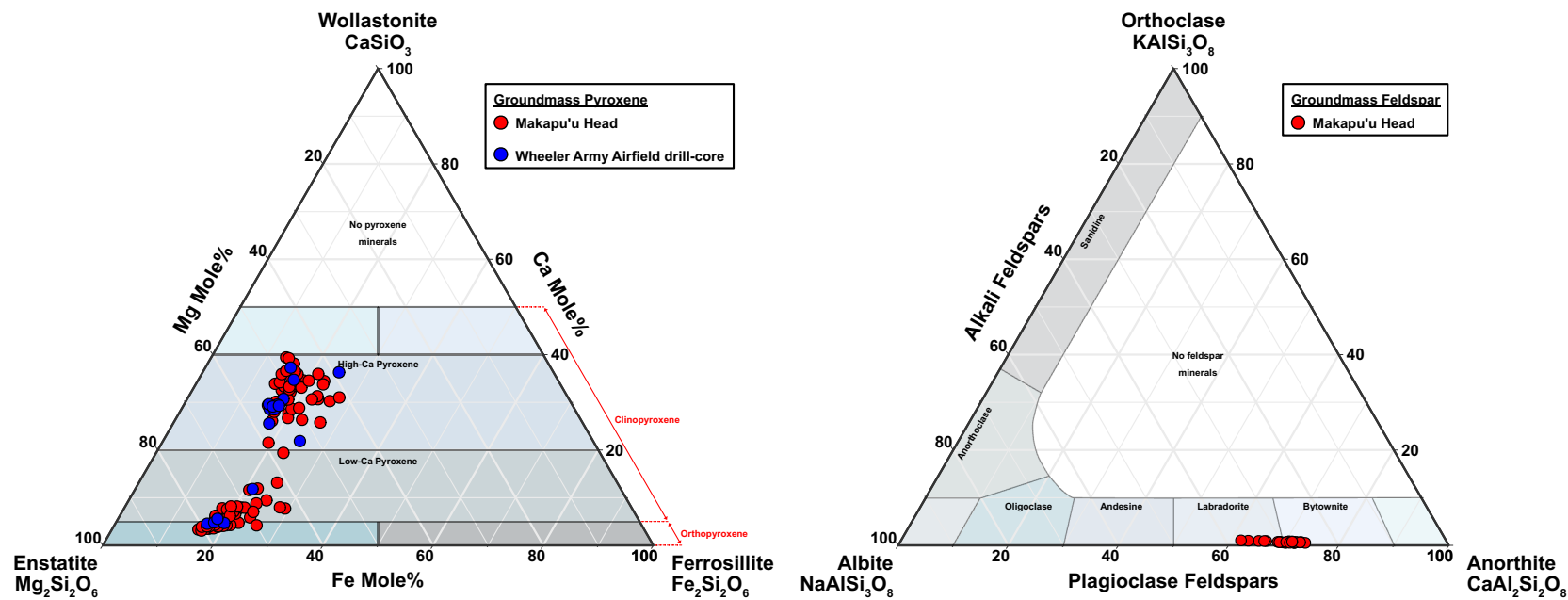


Figure 13: Ternary diagrams of groundmass pyroxene phases (left) and feldspar phases (right). All groundmass feldspar is from sample KOOb-5.

The degree of groundmass crystallinity through the stratigraphic sequence changes at both localities. At Makapu‘u Head, where there is a higher sample resolution, there is a cyclic finer to coarser grained sequence in which groups of samples alternate between finer grained, intersertal (Figure 12B) and coarser grained, intergranular groundmass (Figure 12A) over roughly 30 – 40 m, or over 2 – 4 lava flows. A similar range of crystallinity was observed in the Wheeler Army Airfield drill-core samples, but the sample resolution was too low to determine if there was a similar cyclic trend.

3.1.2 Olivine

Only one sample completely lacks olivine, either as a macrocryst (grains $> 100\ \mu\text{m}$) or groundmass phase: sample WH-563, near the bottom of the Wheeler Army Airfield drill-core (31.48 m.a.s.l.). In all other samples, olivine occurs as the dominate macrocryst, many times with small spinel inclusions. In samples where olivine is present, most contain olivine macrocrysts and antecrysts with alteration rims of iddingsite of varying thicknesses (20 – 60 μm) and smaller olivine macrocrysts that are nearly or completely altered to iddingsite (Figure 14B and 14D). Notably, KOOb-4A (21.61 m.a.s.l.) is the only sample in the entire suite that contains no olivine alteration. KOOb-8 (122.79 m.a.s.l.) is the only sample with large macrocrysts ($>1000\ \mu\text{m}$) that have been altered to saponite (sometimes referred to as bowlingite) rather than iddingsite (Figure 14A and 14C), although not all olivine macrocrysts in this sample are altered to saponite. Notably, KOOb-8 also contains macrocrysts with relatively low alteration of olivine to iddingsite as well as microphenocrysts and groundmass olivine that are completely altered to iddingsite, suggesting that the saponite-altered olivine may have been altered before being entrained in the magma that erupted to form this lava flow. Due to the degree of alteration, olivine macrocryst

rim compositions described henceforth were measured as close to the rim as possible, without incorporating beam volume contamination from the alteration rim.

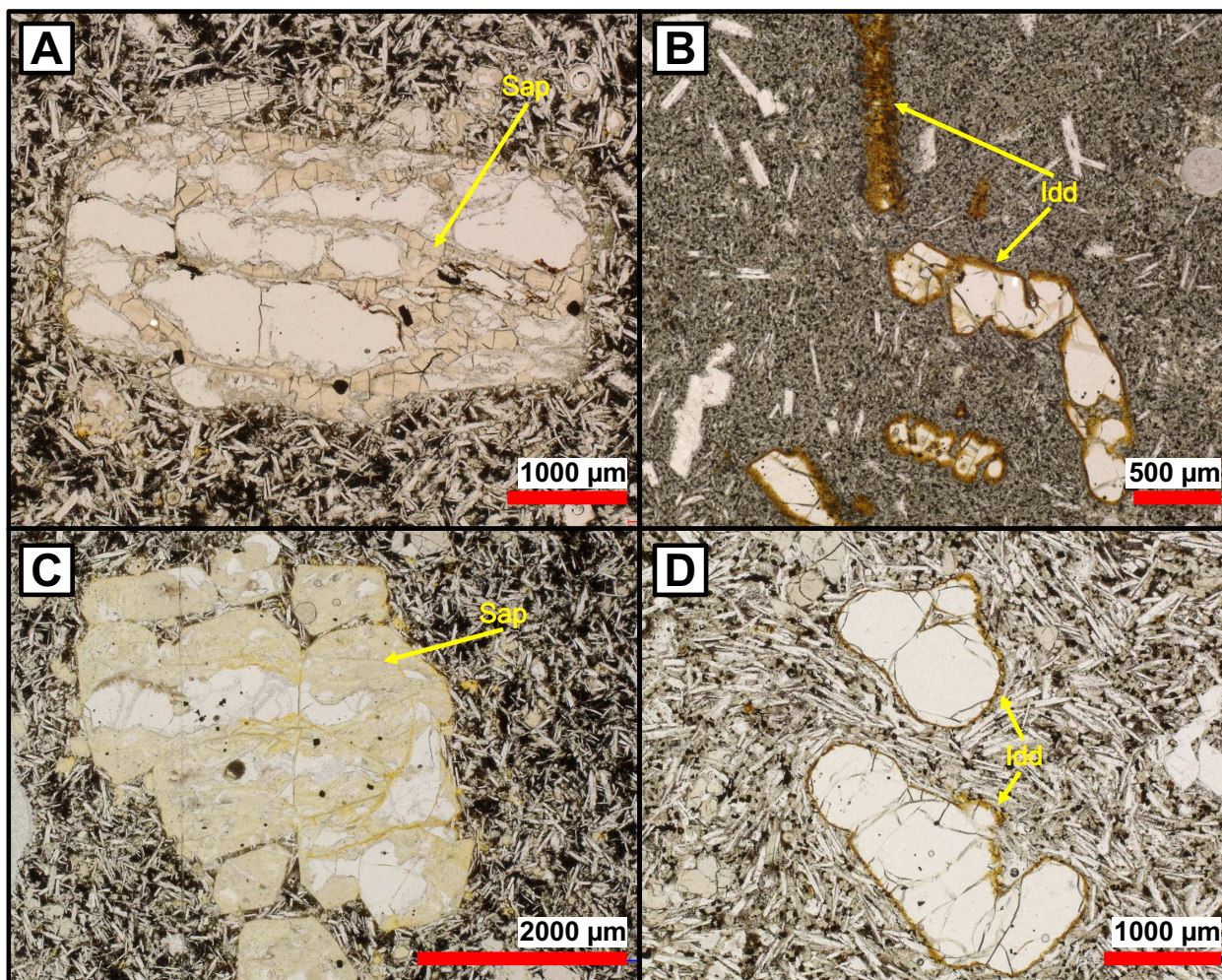


Figure 14: Photomicrographs in plane-polarized light showing alteration products of olivine macrocrysts. A) Olivine altering to saponite, B) olivine with rims of iddingsite alteration, C) olivine glomerocryst altering to saponite, and D) olivine glomerocryst with rim of iddingsite alteration. For phases, Sap = saponite and Idd = iddingsite.

Olivine zoning is determined based on Fo variation that is outside of established analytical error (see section 2.4.2). Some grains have core and rim compositions within analytical error of each other and are thus unzoned ($n = 22$ of 111 analyzed grains). Most olivine macrocrysts are normally zoned ($n = 88$), with an average of 3.76% difference between the

forsterite content of the rims versus the cores. Rims of normally zoned olivine grains range from Fo₇₆ – Fo₈₈ while cores range from Fo₇₉ – Fo₉₀. There is only one reversely zoned olivine macrocryst (WH-636) and it is large (~3350 µm) and heavily resorbed. There is only a 1.90% difference between the forsterite content of the rim and the forsterite content of the core (rim is Fo₈₅ while the core is Fo₈₄). Other large and/or heavily resorbed macrocrysts do not exhibit reverse zoning.

Based on macrocryst transects from core to rim, two olivine macrocrysts exhibit more complex zoning (Figure 15A; colored lines). The crystals display an overall decrease in Fo from core to rim, however, the lowest Fo is displayed in the mantle of the macrocryst (Figure 15A). It is important to note that olivine transects exclude iddingsite alteration rims, and such, 0 µm does not reflect the true rim of each macrocryst.

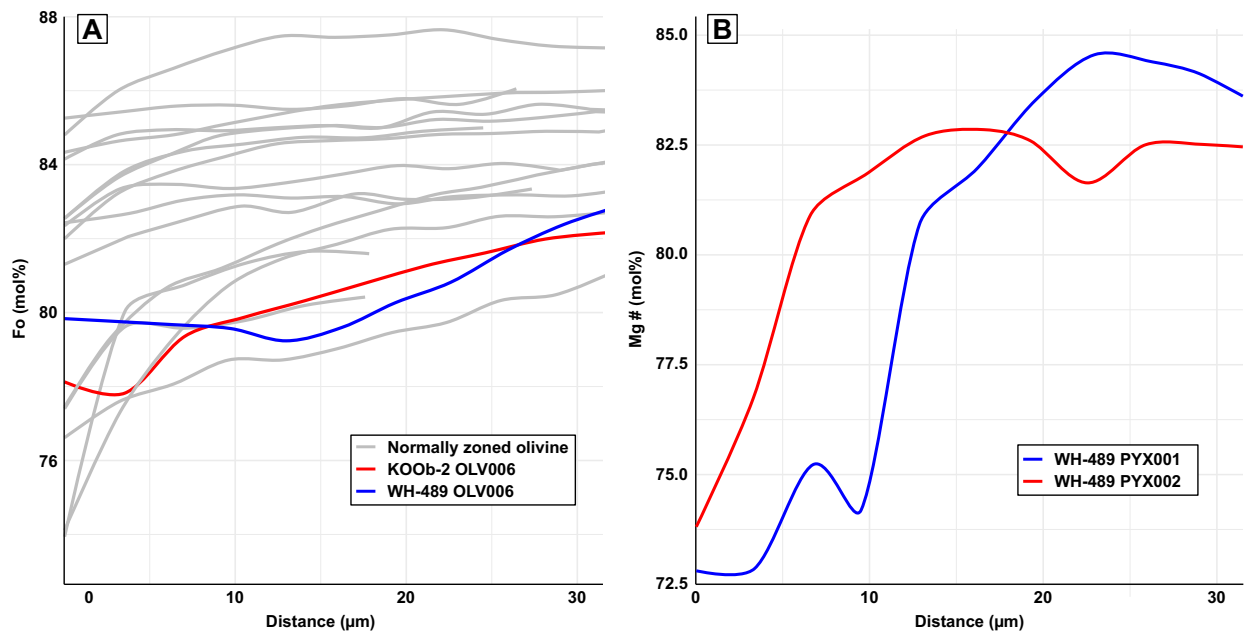


Figure 15: Plot of macrocryst rim-core transects with EPMA points spaced 3 microns apart showing A) Olivine Fo mol% with distance in microns normalized to exclude iddingsite alteration rims and red and blue lines show complexly zoned olivine, and B) Orthopyroxene Mg# mol%. 0 microns represents the rim of the phenocryst.

The morphologies of normally zoned, reversely zoned, and unzoned crystals are quite diverse (Figure 16), and thus, we divide our populations of olivine into 6 groups based on textural variety rather than chemical heterogeneity. Group 1 olivine are large ($\geq 1000 \mu\text{m}$) subhedral to euhedral macrocrysts, notably with very little resorption textures.

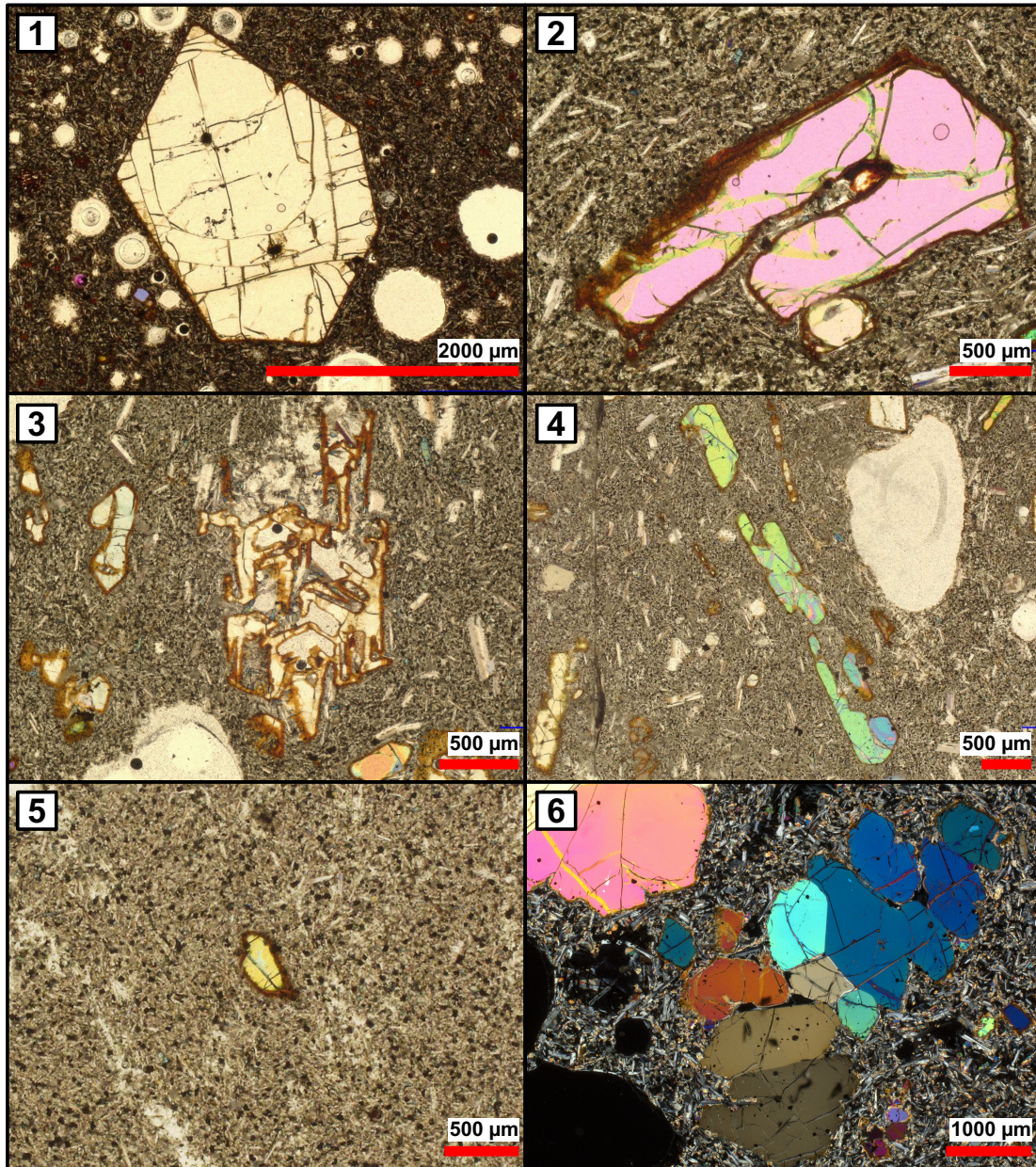


Figure 16: Photomicrographs in cross-polarized light showing various olivine populations, 1) large subhedral-euhedral macrocrysts, 2) heavily resorbed olivine, 3) skeletal olivine, 4)

elongated olivine with resorption textures, 5) small subhedral, rounded macrocrysts, and 6) olivine monomineralic glomerocrysts.

Group 2 olivine are both medium-sized and large (~500 to > 1000 μm) antecrysts that are heavily resorbed, with large embayments and/or very rounded edges. Group 3 olivine are both medium-sized and large (~500 to > 1000 μm) skeletal macrocrysts with dendritic morphologies, including some with enclosed pockets of groundmass parallel to crystal faces. Group 4 olivine are elongated (~500 to > 1000 μm long) and are heavily resorbed, so much so that they are broken into multiple fragments. Group 5 olivine are much smaller (30 – 500 μm) subhedral macrocrysts with very little resorption textures. Group 6 olivine are subhedral to euhedral macrocrysts that range in size from ~500 to > 1000 μm and occur as monomineralic glomerocrysts. Photomicrographs of each textural group are summarized in Figure 16. Group 1, Group 3, and Group 5 olivine are considered macrocrysts that possibly crystallized from the primary melt, due to the lack of resorption textures. However, it cannot be ruled out that these are not antecrysts, due to presence of orthopyroxene reaction rims (see section 3.1.5). Thus, we use the size determining language of macrocrysts rather than phenocryst, to eliminate any genetic origin from their nomenclature. Group 2, Group 4, and Group 6 olivine are considered antecrysts that were likely picked up from the cumulate mush due to the strong resorption textures.

There is no apparent relationship between olivine morphology and stratigraphic order. Where olivine macrocrysts are abundant (e.g. KOOB-15, WH-636, MHSep7-4), many of the morphologies are coincident. Where olivine macrocrysts are not dominant, Group 5 morphologies dominate.

3.1.3 Pyroxene

Subordinate to olivine, pyroxene is present as the next most abundant phenocryst type. Orthopyroxene ($\text{Wo} < 5 \text{ mol\%}$) is the dominant pyroxene phenocryst present (Figure 17).

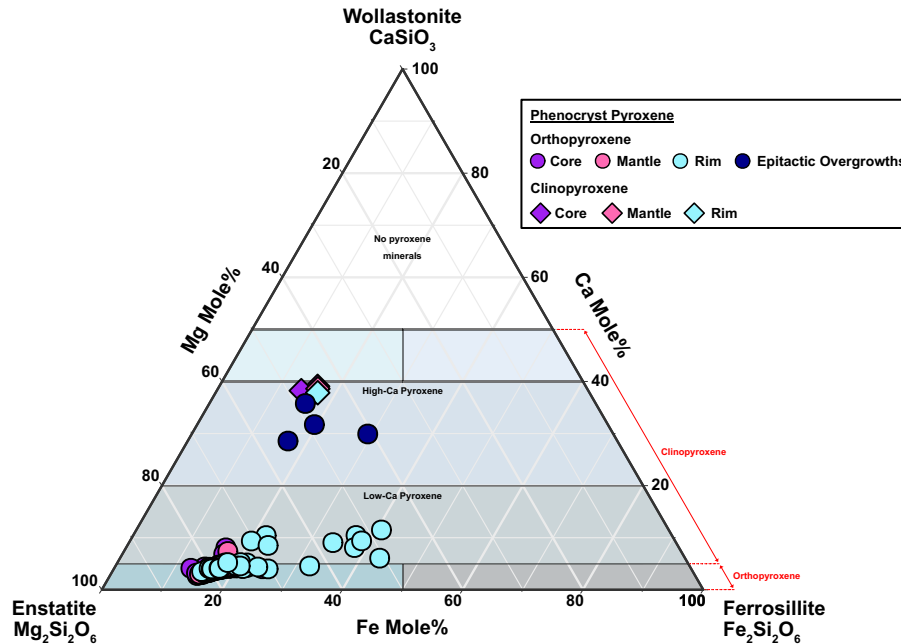


Figure 17: Ternary diagram of pyroxene phenocryst core, mantle, rims, and in the case of orthopyroxene, epitactic overgrowths, for Makapu'u Head and Wheeler Army Airfield drill-core.

Orthopyroxene phenocrysts are unaltered, subhedral to euhedral crystals that range in size from 200 to 1000 μm or greater. Orthopyroxene are present as phenocrysts (Group 1), monomineralic glomerocrysts (Group 2), and polymineralic glomerocrysts with plagioclase (Group 3), summarized in Figure 18. Some orthopyroxene phenocrysts display disequilibrium textures like rounded edges but overall do not exhibit strong disequilibrium textures. Orthopyroxene transects reveal complex zoning, with Mg# increasing and decreasing drastically from core to rim, but overall decreasing from core to rim (Figure 15). Overall, cores of orthopyroxene phenocrysts vary from Mg#₇₄ – Mg#₈₇, and rims vary from Mg#₅₄ – Mg#₈₄.

Five clinopyroxene macrocrysts were found ($\text{Wo} > 5 \text{ mol}\%$), three of which are pigeonite, or low-Ca clinopyroxenes ($5 \text{ mol}\% < \text{Wo} < 20 \text{ mol}\%$). These pigeonite macrocrysts are elongated, $\sim 50 \mu\text{m}$ wide crystals encased by high-Ca clinopyroxene. Many orthopyroxene phenocrysts with clinopyroxene reaction rims contain pigeonite compositions in the intermediate

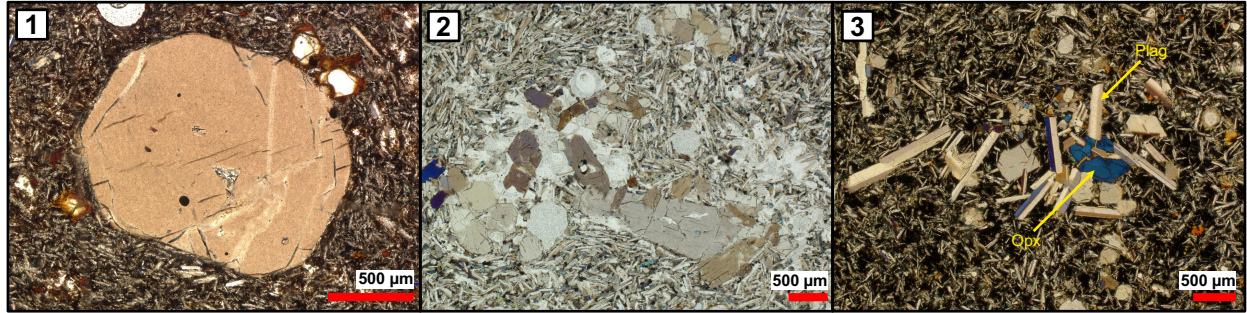


Figure 18: Photomicrographs in cross-polarized light of orthopyroxene phenocrysts showing variety in morphologies, with 1) group of subhedral-euhedral phenocrysts, 2) monomineralic glomerocrysts, and 3) polymineralic glomerocrysts with plagioclase. For phases, Plag = plagioclase feldspar and Opx = orthopyroxene.

zone between the core and rim, interpreted to be a result of diffusion between the high-Ca rim and low-Ca core. Thus, these pigeonite macrocrysts display a similar transition of increasing Ca from core to rim, and thus, are likely orthopyroxene phenocrysts that have almost completely diffused into a pigeonite composition. Only two high-Ca clinopyroxene ($Wo > 20$ mol%) macrocrysts were found in the entire sample suite. One exhibits a thick reaction rim of orthopyroxene, indicating strong disequilibrium (Figure 19A), while the other is euhedral, but is fractured (Figure 19B). Thus, these two high-Ca clinopyroxenes are considered antecrysts. Cores of the high-Ca clinopyroxene antecrysts are $Mg\#_{73}$ and $Mg\#_{77}$, respectively.

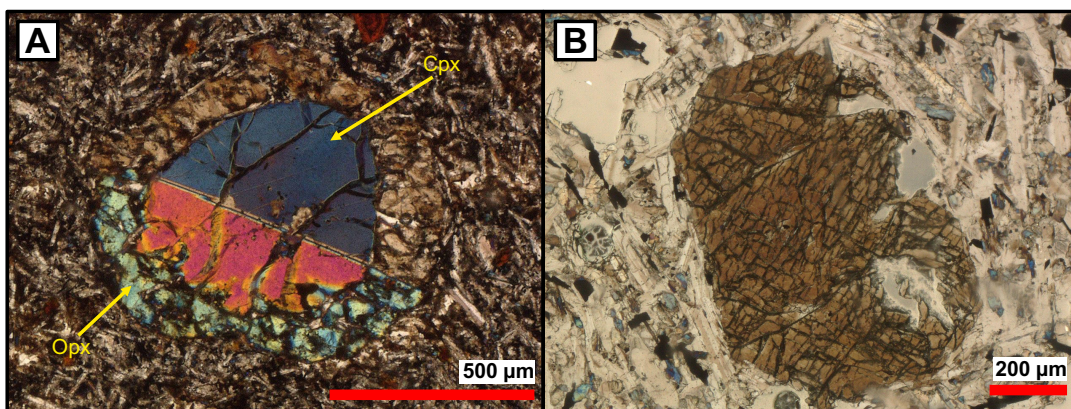


Figure 19: Photomicrographs in cross-polarized light of high Ca clinopyroxene antecrysts from A) sample WH-541 showing an orthopyroxene reaction rim on the clinopyroxene antecryst and

B) the heavily fractured clinopyroxene antecryst in sample WH-563. For phases, Cpx = clinopyroxene and Opx = orthopyroxene.

3.1.4 Plagioclase

Plagioclase is the least abundant phenocryst phase, present in small amounts or not at all, depending on the sample. Texturally, plagioclase are 500 to 1000 μm or greater, tabular, present as euhedral phenocrysts (Group 1), anhedral to subhedral phenocryst with rounded edges (Group 2), monomineralic glomerocrysts (Group 3), and polymineralic glomerocrysts with orthopyroxene (Group 4), summarized in Figure 20. Only groundmass plagioclase and inclusions within pyroxene phenocrysts within sample KOOB-5 were analyzed. Groundmass plagioclase display anorthite compositions ranging from An_{62} – An_{74} and inclusions range from An_{68} – An_{71} .

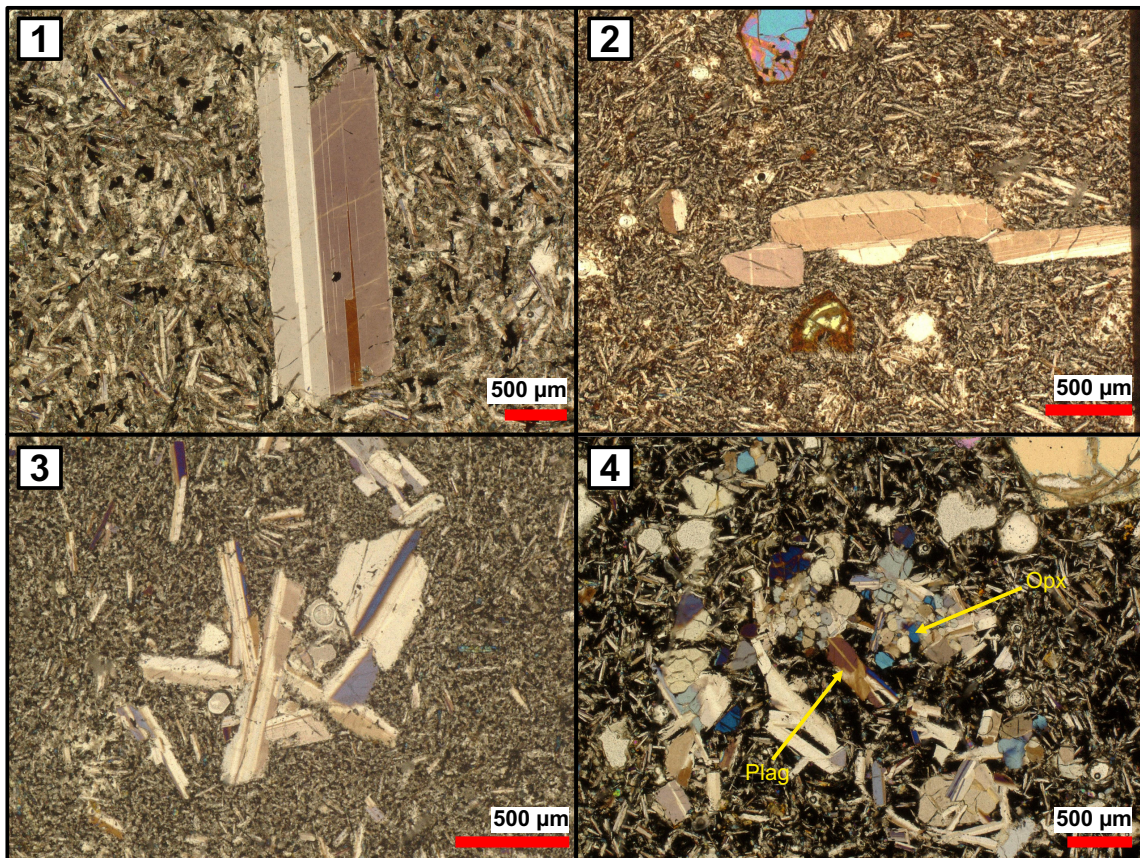


Figure 20: Photomicrographs in cross-polarized light of plagioclase phenocrysts showing a variety in morphologies, with 1) euhedral, tabular phenocryst, 2) anhedral, rounded grains, 3)

monomineralic glomerocrysts, and 4) polymineralic glomerocrysts with orthopyroxene. For phases, Plag = plagioclase feldspar and Opx = orthopyroxene.

3.1.5 Pyroxene Reaction Rims

All samples show disequilibrium textures to varying degrees such as resorption and embayments of olivine, pyroxene, and plagioclase phenocrysts. In most samples, both pyroxene and olivine grains show pyroxene reaction rims. Olivine is commonly heavily resorbed, with sawtooth edges and pyroxene reaction rims (Figure 21). Iddingsite alteration rims commonly form on the olivine-reaction rim margin, indicated by brighter colors in BSE (Figure 21A and 21B). This is likely an effect of post-emplacement weathering where meteoric water can seep

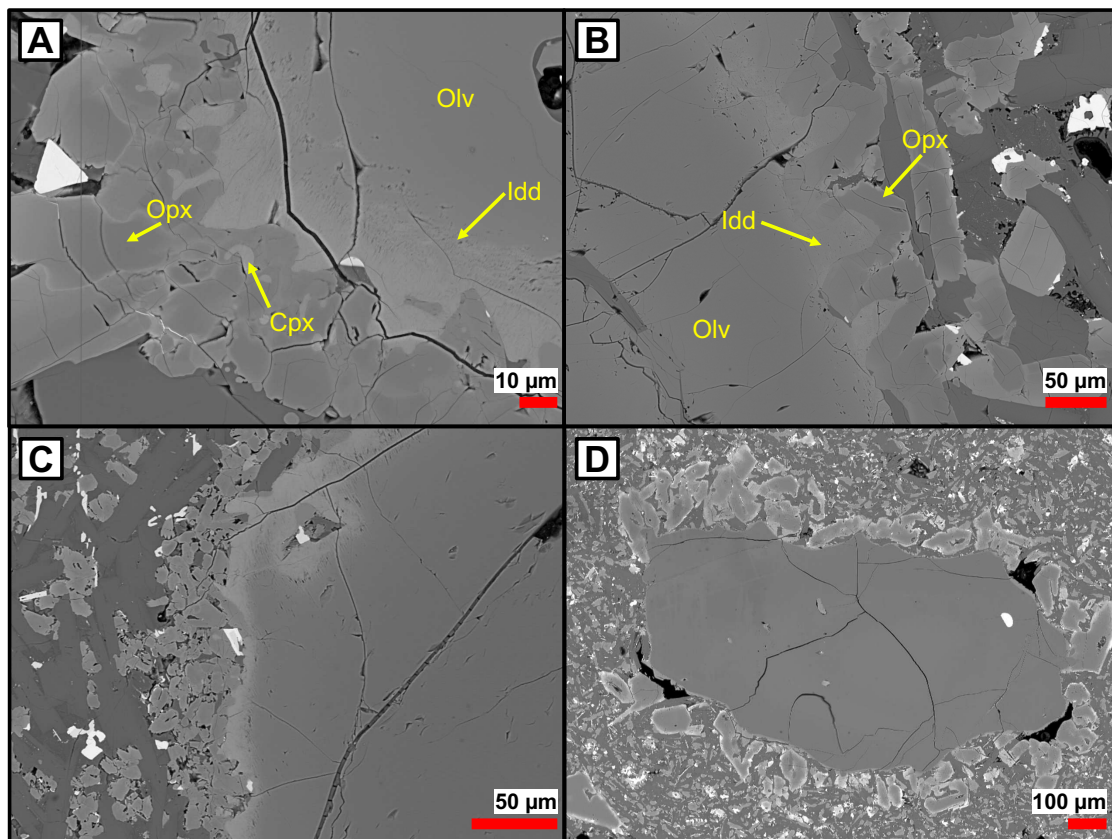


Figure 21: BSE images of olivine macrocryst showing variety in pyroxene reaction rim morphologies and iddingsite alteration rims. A,B) shows pyroxene reaction rims that continue the crystal habit of the heavily resorbed olivine C,D) shows pyroxene rims where the pyroxene has defined crystal boundaries. In all panels, varying grayscale in reaction rims depict intergrown

low-Ca (darker) and high-Ca (lighter) pyroxene. For phases, Olv = olivine, Opx = orthopyroxene, Cpx = clinopyroxene, and Idd = iddingsite.

between the reaction rim crystal boundaries to alter olivine, which is more susceptible to low temperature alteration than pyroxene. The morphology of pyroxene reaction rims on olivine follow a continuum from thicker (~100 μm) rims of pyroxene with more defined crystal boundaries (Figure 21D) to thinner (~ 50 μm or less), amorphous, epitactic rims of pyroxene that continue the crystal habit of the heavily resorbed olivine (Figure 21B). Reaction rims on olivine vary between these two endmembers of morphologies (Figure 21A and 21C), although rims thicker than 100 μm are less abundant. Within the same olivine grain, a single reaction rim may contain areas of orthopyroxene, low-Ca clinopyroxene, and high-Ca clinopyroxene intergrown together (Figure 21A). Reaction rims on olivine are dominantly low-Ca clinopyroxene (Figure 22; 71 of 88 total analyzed rim crystals).

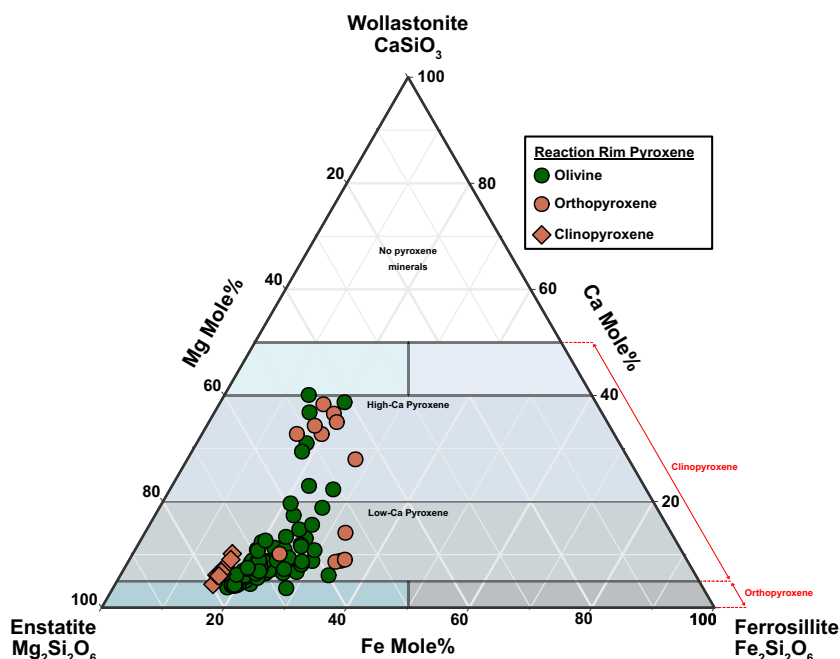


Figure 22: Ternary diagram showing chemistry of pyroxene reaction rims on olivine, orthopyroxene, and clinopyroxene for Makapu‘u Head and Wheeler Army Airfield. This does not include any epitactic overgrowth rims on orthopyroxene (see Figure 23A).

Orthopyroxene phenocrysts dominantly exhibit epitactic growth morphology (Nicholls and Stout, 1997, Winslow et al., 2025), changing from an orthopyroxene core to a low-Ca or high-Ca clinopyroxene rim (Figure 23A). Sample WH-563 (31.48 m.a.s.l.) is the only sample in which orthopyroxene phenocrysts have crystalline reaction rims of low-Ca and high-Ca clinopyroxene (Figure 23B, Figure 22). Nonetheless, grains with rims of high-Ca clinopyroxene commonly also have compositions of pigeonite, or low-Ca clinopyroxene, in the intermediate zone between the core and rim, likely as a diffusion product between the orthopyroxene core and high-Ca clinopyroxene rim (Figure 17).

One of the two high-Ca clinopyroxene antecrysts found displays a thick reaction rim of orthopyroxene and low-Ca clinopyroxene with defined pyroxene crystal boundaries (Figure 23C and 23D). The other high-Ca clinopyroxene antecryst found does not have an overgrowth rim or change of pyroxene phase towards the rim (Figure 23E and 23F). Chemically, the pyroxene rims found on olivine macrocrysts and antecrysts are similar to the rims on clinopyroxene antecrysts and orthopyroxene phenocrysts, although the morphologies vary greatly (Figure 22).

Epitactic overgrowth of clinopyroxene on orthopyroxene is ubiquitous among samples, while few samples do not display pyroxene reaction rims on olivine macrocrysts: KOOB-12B (183.61 m.a.s.l.), KOOB-8 (122.79 m.a.s.l.), and KOOB-4A (21.61 m.a.s.l.). The abundance and thickness of pyroxene overgrowth rims tend to correlate with the abundance of orthopyroxene phenocrysts in the sample. Samples KOOB-10 (141.85 m.a.s.l.), KOOB-16 (78.85 m.a.s.l.), KOOB-5 (30.67 m.a.s.l.), WH-489 (54.48 m.a.s.l.), and WH-563 (31.48 m.a.s.l.) all have more orthopyroxene relative to olivine, and all display thick pyroxene reaction rims of various morphologies on both olivine macrocrysts, orthopyroxene phenocrysts, and clinopyroxene antecrysts. One exception is sample KOOB-8 (122.79 m.a.s.l.), which has more orthopyroxene

relative to olivine, but does not display any pyroxene reaction rims on olivine macrocrysts or antecrysts.

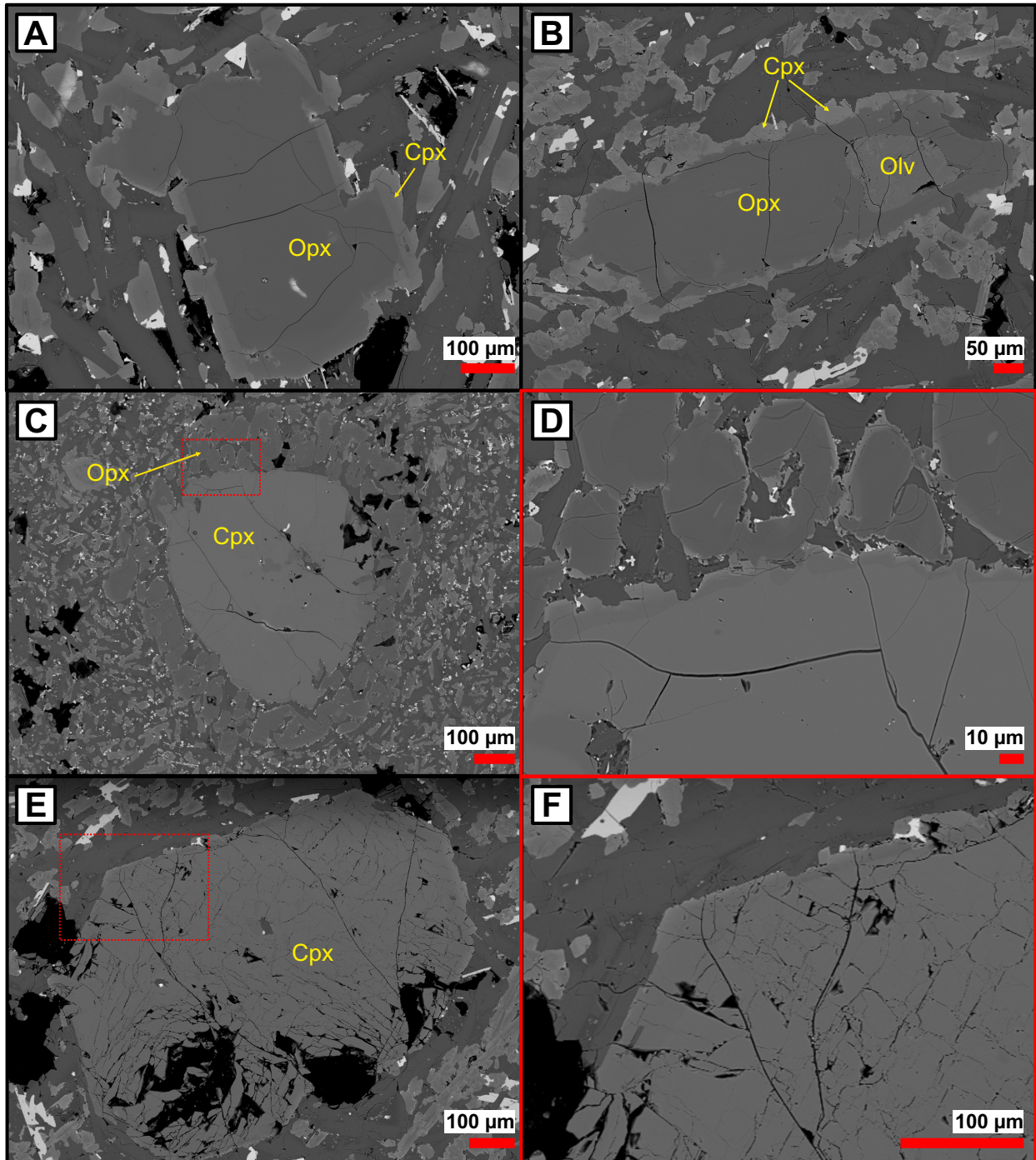


Figure 23: BSE images of pyroxene showing A) orthopyroxene phenocryst with epitactic overgrowth of clinopyroxene, B) orthopyroxene phenocryst with crystalline clinopyroxene

reaction rim, C & D) clinopyroxene antecryst with rim of distinct orthopyroxene crystals, E & F) heavily fractured clinopyroxene antecryst with no reaction rim. For phases, Opx = orthopyroxene, Cpx = clinopyroxene, and Olv = olivine.

3.2 Weka Trainable Segmentation Phase Mapping

Mineral phase abundances from WTS phase mapping are summarized in Table 3.

Table 3: Summary of Weka Trainable Segmentation phase mapping results of samples from Makapu'u Head and Wheeler Army Airfield drill-core, in order of stratigraphic level. For phases, olv = olivine, plag = plagioclase, pyx = pyroxene.

<i>Sample</i>	<i>Elevation (m.a.s.l.)</i>	<i>Olv%</i>	<i>Plag%</i>	<i>Pyx%</i>	<i>Vesicle %</i>	<i>Oxide %</i>	<i>Groundmass %</i>
<i>Makapu 'u Head</i>							
KOOb-14	196.79	0.59%	/	/	36.56%	1.50%	61.35%
KOOb-12B	183.61	2.56%	0.75%	1.33%	7.31%	/	88.04%
KOOb-15	168.07	10.58%	2.09%	1.53%	2.70%	/	83.10%
KOOb-16	78.86	0.29%	/	0.09%	4.76%	2.83%	92.03%
KOOb-5	30.67	1.84%	/	3.00%	6.61%	/	88.56%
MH-Sep7-4	21.59	22.95%	/	/	12.71%	/	64.34%
KOOb-2	5.75	0.17%	/	0.30%	10.79%	0.29%	88.45%
<i>Wheeler Army Airfield drill-core</i>							
WH-489	54.48	0.83%	4.14%	/	1.96%	5.08%	87.99%
WH-541	38.48	5.50%	0.95%	0.48%	8.25%	/	84.82%
WH-636	9.48	10.97%	/	0.04%	18.32%	/	70.67%

Where macrocrysts are present, modal percentages of olivine varied between 0.17 and 22.95%, pyroxene between 0.04 and 3.00%, plagioclase between 0.75 and 4.14%, oxides between 0.29 and 5.08%, vesicles between 1.96 and 36.56%, and groundmass between 61.35 and 92.03%. There is no trend between modal percentages or vesicle abundance and stratigraphic order (Figure 24).

3.3 Comparison to Literature EPMA Data & Other Hawaiian Volcanoes

3.3.1 Olivine

Trace element compositions for olivine macrocrysts and antecrysts measured in this study are compared to published compositions for Ko'olau Volcano and other Kea- and Loa-trend Hawaiian volcanoes (Kīlauea, Mauna Loa, Mauna Kea, Haleakalā, Hualālai, Wai'anae, and Kaua'i). NiO wt.% for olivine macrocrysts and antecrysts measured in this study range from 0.19

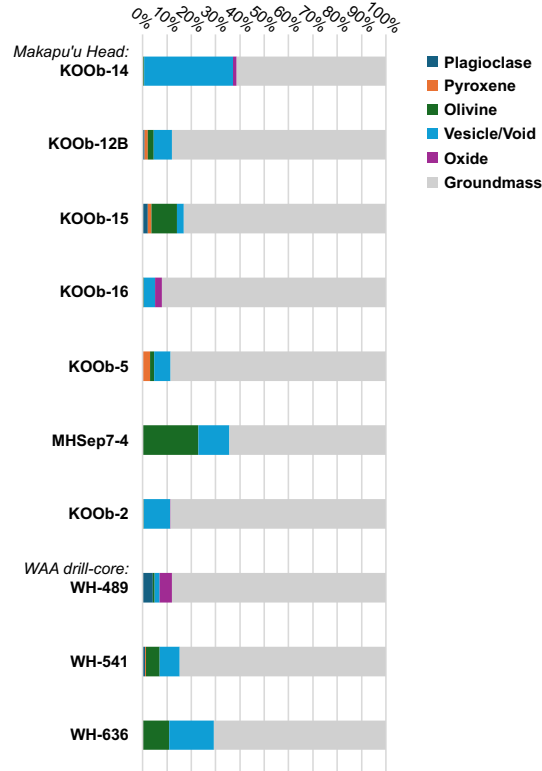


Figure 24: Bar plot of mineral phase abundances for Makapu'u Head and Wheeler Army Airfield (WAA) drill-core samples, in stratigraphic order.

- 0.52%. Our data plots within the range of other Loa-trend volcanoes and literature Ko‘olau data (Figure 25A). Outliers of high NiO wt.% at a given Fo% exist in the literature subaerial Ko‘olau-Makapu‘u dataset and subaqueous Nu‘uanu Landslide dataset, however, we do not see these same high-Ni outliers in our data, which spans the entire stratigraphic section of the exposed Makapu‘u Head (Figure 25). CaO wt.% for data in this study ranges from 0.15 - 0.25%, plotting in the range of subaerial Ko‘olau-Makapu‘u data but on the low-end of data from Loa-trend volcanoes and samples from the subaqueous Nu‘uanu Landslide (Figure 25B). The Nu‘uanu Landslide dataset includes both early main stage Ko‘olau basalts (Loa-trend) and late main stage Ko‘olau-Makapu‘u basaltic andesites (Enriched Loa), thus these higher Ca Nu‘uanu samples reflect Loa-type compositions (Garcia, 2002). MnO wt.%, Al₂O₃ wt.%, and Cr₂O₃ wt.% data from this study overlap with published Ko‘olau data and other Loa-trend volcanoes (Figure 25).

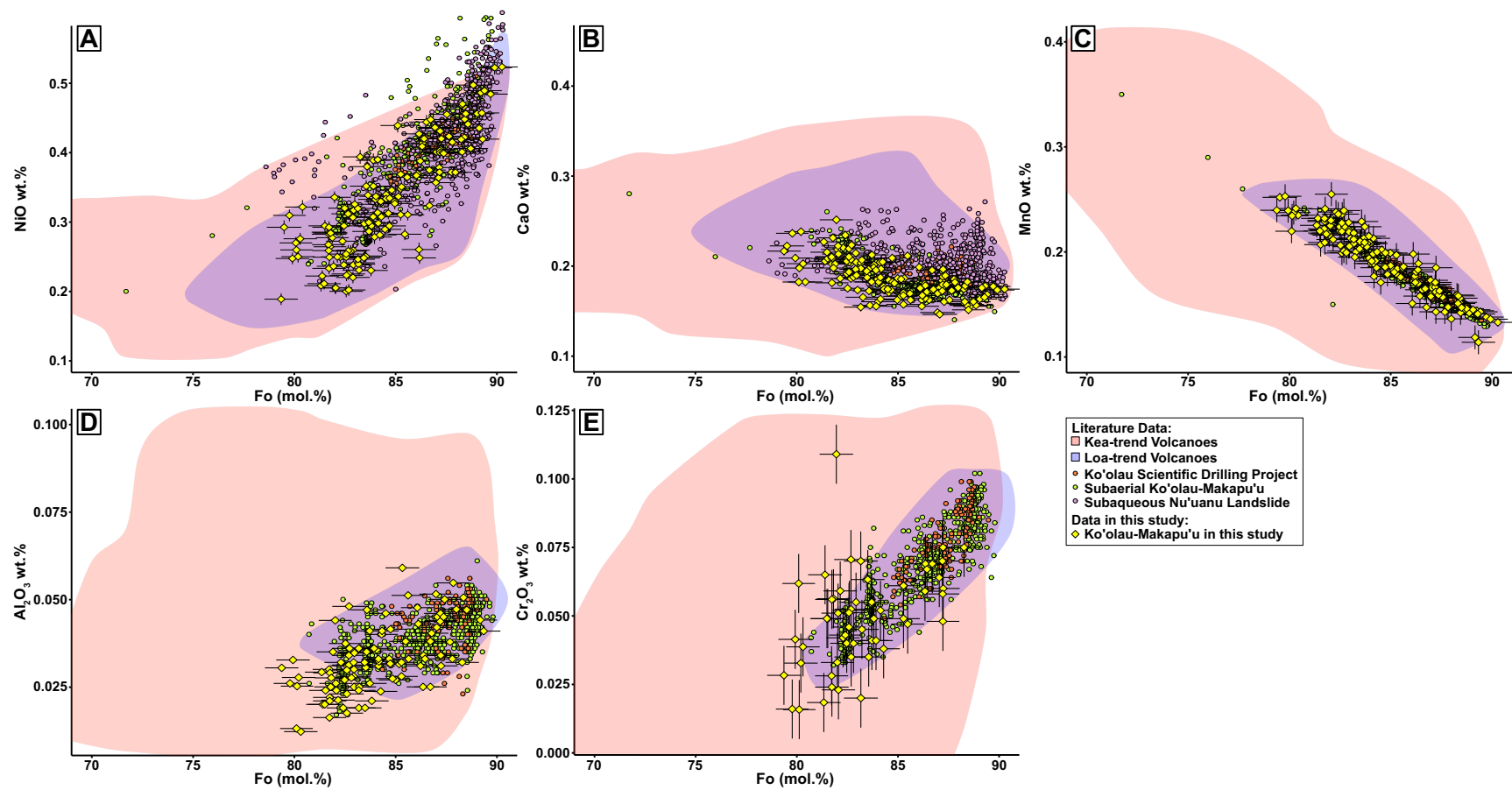


Figure 25: Plots of core macrocryst and antecryst trace element compositions for olivine in wt.% vs. forsterite content in mol.% collected via EPMA for both published data and data reported in this study. Shaded areas are approximate fields for Kea-trend compositions (Kīlauea, Mauna Kea, and Haleakalā) and Loa-trend compositions (Mauna Loa, Hualālai, Wai‘anae, and Kaua‘i). Horizontal and vertical error bars represent calculated error reported in Supplementary Information A, Table 2.

NiO concentrations in Ko‘olau-Makapu‘u basaltic andesites have been described as systematically higher than other Loa- and Kea-trend volcanoes, which has been used to argue for the presence of pyroxenite or eclogite in the mantle source (Sobolev et al., 2005 & 2007). Although high-NiO olivine is the foundation of the argument for the presence of lithologic heterogeneity in the Hawaiian mantle source, there is a lack of published olivine EPMA data for Ko‘olau-Makapu‘u. In fact, the only olivine EPMA data that currently exist for Ko‘olau-Makapu‘u are from Sobolev et al. (2007), Sakyi et al. (2012), Weinstein et al. (2004), and Ireland et al. (2009). It is possible that other Nu‘uanu EPMA datasets (e.g. Garcia, 2002) may contain Ko‘olau-Makapu‘u lavas in their analyses, but without stratigraphic context it is difficult to say with certainty. Nonetheless, the current olivine EPMA dataset for Ko‘olau-Makapu‘u is remarkably small. Sobolev et al. (2007) encompasses 94.55% of the current olivine EPMA dataset for Ko‘olau-Makapu‘u (Supplementary Information A, Table 8). However, all 590 olivine analyses in Sobolev et al. (2007) are from 8 samples: 4 from Makapu‘u Head, 2 from Kamehame Ridge, and 2 unpublished samples with unclear sample locations. This study provides, for the first time, a full, geologically constrained stratigraphic suite of Ko‘olau-Makapu‘u lava flows from two main locations on O‘ahu: Makapu‘u Head ($n = 15$) and Wheeler Army Airfield drill-core ($n = 6$). Furthermore, Sobolev et al. (2007) considered only highly magnesian olivine ($\text{Fo mol\%} > 86$). It is possible that this high-Fo filter biases their dataset and does not account for the full breadth of olivine compositions in the Ko‘olau-Makapu‘u suite as this thesis does. This thesis reports olivine macrocryst core Fo mol% as low as 78%. This study increases the number of Ko‘olau Makapu‘u samples with olivine analyses from 22 samples in the literature data to 41, an increase of 53.66%. Thus, with this more representative dataset, we statistically analyze how

Ko‘olau-Makapu‘u trace element compositions (NiO, MnO, and CaO) compares to other Hawaiian volcanoes.

Statistical comparison run #1 compared Ko‘olau-Makapu‘u lavas (both literature data and data in this thesis) to published data for other Hawaiian volcanoes. This run yielded a statistically significant difference in NiO wt.%, MnO wt.%, and CaO wt.% with p-values $< 2.2 \times 10^{-16}$ in all cases. This value is significantly less than our significance level of 0.05, thus, we can reject the null hypothesis and state that there is a statistically significant difference in these trace element compositions. R-values for NiO wt.%, MnO wt.%, and CaO wt.%, respectively are 0.418, 0.254, and 0.761. Thus, there is a moderate difference in NiO wt.%, small difference in MnO wt.%, and large difference in CaO wt.% between both measured and published Ko‘olau-Makapu‘u data and other published Hawaiian volcano data. This is consistent with the lithologic heterogeneity model outlined in Sobolev et al. (2005, 2007).

Statistical comparison run #2 compared Ko‘olau-Makapu‘u lavas (only data measured in this thesis) to published data for other Hawaiian volcanoes. Published Ko‘olau-Makapu‘u data was excluded from this statistical analysis to remove any possible sampling bias from the 590 olivine analyses from Sobolev et al. (2007) while still assessing differences in trace element compositions between volcanoes. This run yielded p-values of 0.0003 for NiO wt.%, 0.0012 for MnO wt.%, and $< 2.2 \times 10^{-16}$ for CaO wt.%. Thus, in all cases, the trace element compositions are statistically significantly different. R-values for NiO wt.%, MnO wt.%, and CaO wt.% are 0.123, 0.117, and 0.584, respectively. When analyzing only measured data in this thesis against other Hawaiian volcanoes, there is only a small difference in NiO wt.%, small difference in MnO wt.%, and large difference in CaO wt.%.

In both cases (Run #1 and Run #2) there is an established statistically significant difference in NiO wt.%, MnO wt.%, and CaO wt% between Ko‘olau-Makapu‘u lavas and other Hawaiian volcano basalts. However, the degree of this significance varies between runs. To assess why the r-values between runs are different, measured data in this thesis was tested against other published Ko‘olau-Makapu‘u data (Statistical comparison run #3). For this, we find p-values of 1.251×10^{-13} for NiO wt.%, 4.795×10^{-9} for MnO wt.%, and 0.7763 for CaO wt.%. R-values for NiO wt.% and MnO wt.%, respectively, are 0.266 and 0.210. Thus, only NiO wt.% and MnO wt.% is significantly different between data in this thesis and other published Ko‘olau-Makapu‘u data, and this difference is small.

Due to the large r-value for CaO wt.% in both Run #1 and #2 (0.761 and 0.584, respectively), and the non-significant difference in CaO wt.% between data in this thesis and published Ko‘olau-Makapu‘u data (p-value = 0.776), we can say that there is a strong statistically significant difference in CaO wt.% between Ko‘olau-Makapu‘u and other Hawaiian volcanoes. Given the statistically significant difference of NiO wt.% and MnO wt.% between data in this thesis and published Ko‘olau-Makapu‘u data we look to Run #2 to assess the comparison of Ko‘olau-Makapu‘u compositions to other Hawaiian volcanoes. Based on the small r-values for each, we can say there is a weak statistically significant difference in NiO wt.% and MnO wt.% between Ko‘olau-Makapu‘u and other Hawaiian volcanoes. Thus, the trend of high NiO wt.% perceived by Sobolev et al. (2005 & 2007) from a small sample size is also present in NiO compositions from samples in this dataset with a larger sample size, although this trend is weak. The statistical analyses are summarized in Figure 26.

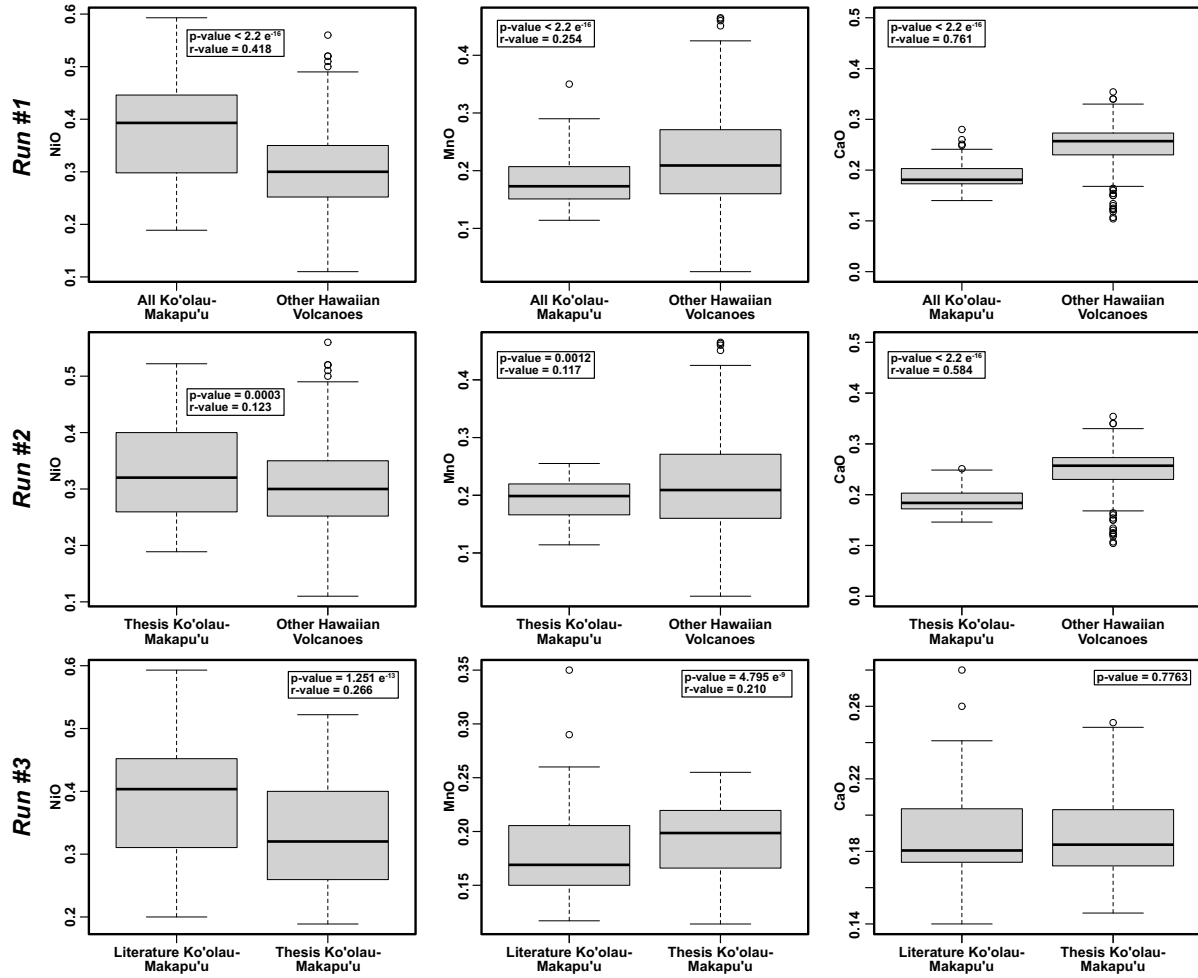


Figure 26: Box plots of NiO wt.%, MnO wt.%, and CaO wt.% concentrations for each statistical analysis. Each inset box displays the p-value and r-value (if applicable) of the statistical analysis.

3.3.2 Pyroxene

Major, minor, and trace element concentrations for pyroxenes measured in this study are compared to published pyroxene compositions for Ko'olau-Makapu'u from Weinstein et al. (2004), and available data from other Loa- and Kea-trend volcanoes (Wai'anae and Kīlauea, respectively). Among major elements, clinopyroxene concentrations show two parallel trend-lines: high-Ca clinopyroxene compositions follow similar FeO wt.% and MgO wt.% at a given Mg# to other Hawaiian volcanoes and low-Ca clinopyroxene compositions follow a trend of higher FeO wt.% and MgO wt.% at a given Mg# (Figure 27). Clinopyroxene MnO wt.%

concentrations also show two parallel trends, one of low-Ca clinopyroxenes and the other of high-Ca clinopyroxenes (Figure 27). Low-Ca clinopyroxenes are also lower in Al₂O₃ wt.% and TiO₂ wt.%, but do not show systematic differences in NiO wt.% and Cr₂O₃ wt.% when compared to high-Ca clinopyroxenes (Figure 27). The same parallel trends of FeO wt.%, MgO wt.%, and MnO wt.% are not observed in orthopyroxene concentrations (Figure 28). However, orthopyroxene concentrations show trends of decreasing FeO wt.%, TiO₂ wt.%, and MnO wt.% and increasing MgO wt.%, Al₂O₃ wt.%, Cr₂O₃ wt.%, and NiO wt.% with increasing Mg# (Figure 28). Phenocrysts and inclusions anchor the trend on the high Mg# end, and groundmass and reaction rims anchor the trend on the low Mg# end, consistent with crystallization of later phases (groundmass and reaction rims) in a later, more evolved system.

3.3.3 Plagioclase

Major, minor, and trace element concentrations of groundmass and inclusion plagioclase in sample KOOb-5 (30.67 m.a.s.l.) are compared to published compositions for Ko‘olau-Makapu‘u from Weinstein et al. (2004) and available data from other Kea- and Loa-trend Hawaiian volcanoes (Kīlauea and Mauna Loa). Al₂O₃ wt.%, CaO wt.%, Na₂O wt.%, FeO wt.%, and MgO wt.% for plagioclase in this study plots within the range of published plagioclase compositions for other Hawaiian volcanoes and Ko‘olau-Makapu‘u (Figure 29).

3.4 Pyroxene Chemical Maps

EPMA maps of two orthopyroxene phenocrysts and one olivine macrocryst with a pyroxene reaction rim from sample KOOb-5 reveal chemical heterogeneity on the mineral scale. The two orthopyroxene phenocrysts (Figure 30 and 31) display oscillatory zonation of CaO wt.%, Al₂O₃ wt.%, and Cr₂O₃ wt.%. Notably, PYX009 shows much stronger concentric zonation, while PYX015 shows less-defined zones of oscillating CaO wt.%, Al₂O₃ wt.%, and Cr₂O₃ wt.%.

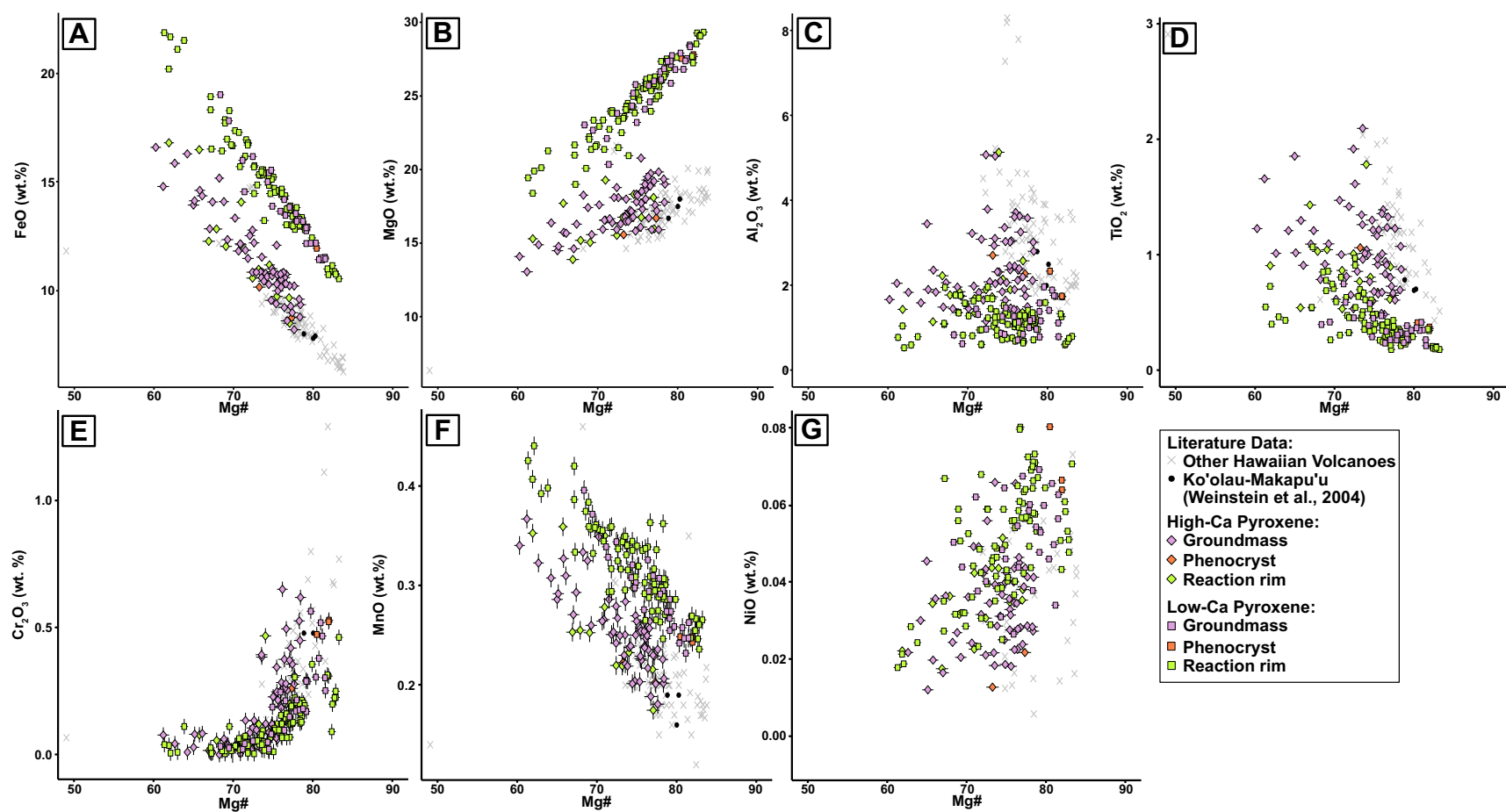


Figure 27: Plots of major, minor, and trace element compositions for low-Ca and high-Ca pyroxenes in wt.% vs. magnesium number in mol.% collected via EPMA for both published data and data reported in this study. Other Hawaiian volcanoes include Kīlauea and Waiʻanae. Phenocryst points depict core compositions. Horizontal and vertical error bars represent calculated error reported in Supplementary Information A, Table 3.

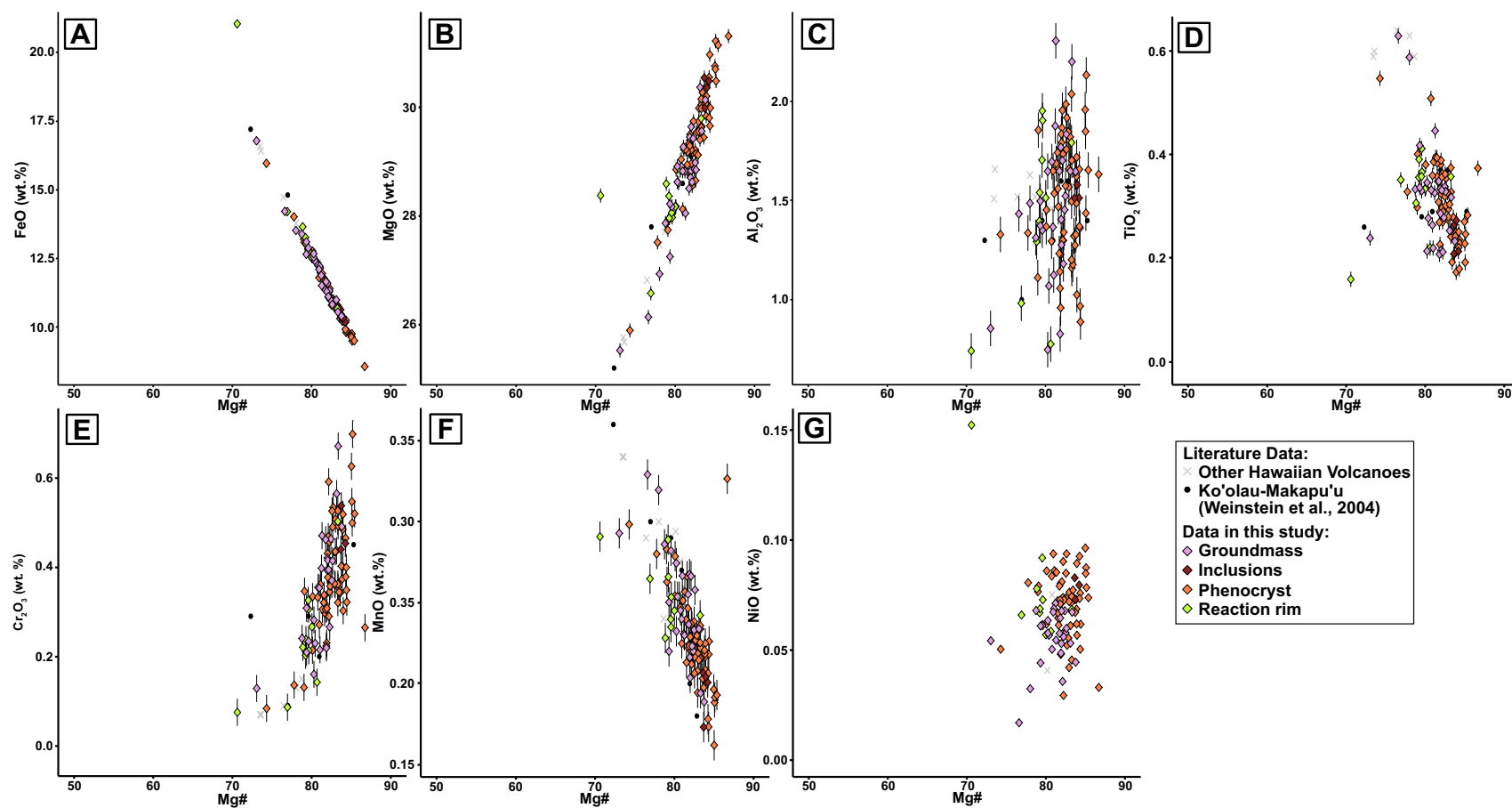


Figure 28: Plots of major, minor, and trace element compositions for orthopyroxenes in wt.% vs. magnesium number in mol.% collected via EPMA for both published data and data reported in this study. Other Hawaiian volcanoes is only Kīlauea. Phenocryst points depict core compositions. Horizontal and vertical error bars represent calculated error reported in Supplementary Information A, Table 3.

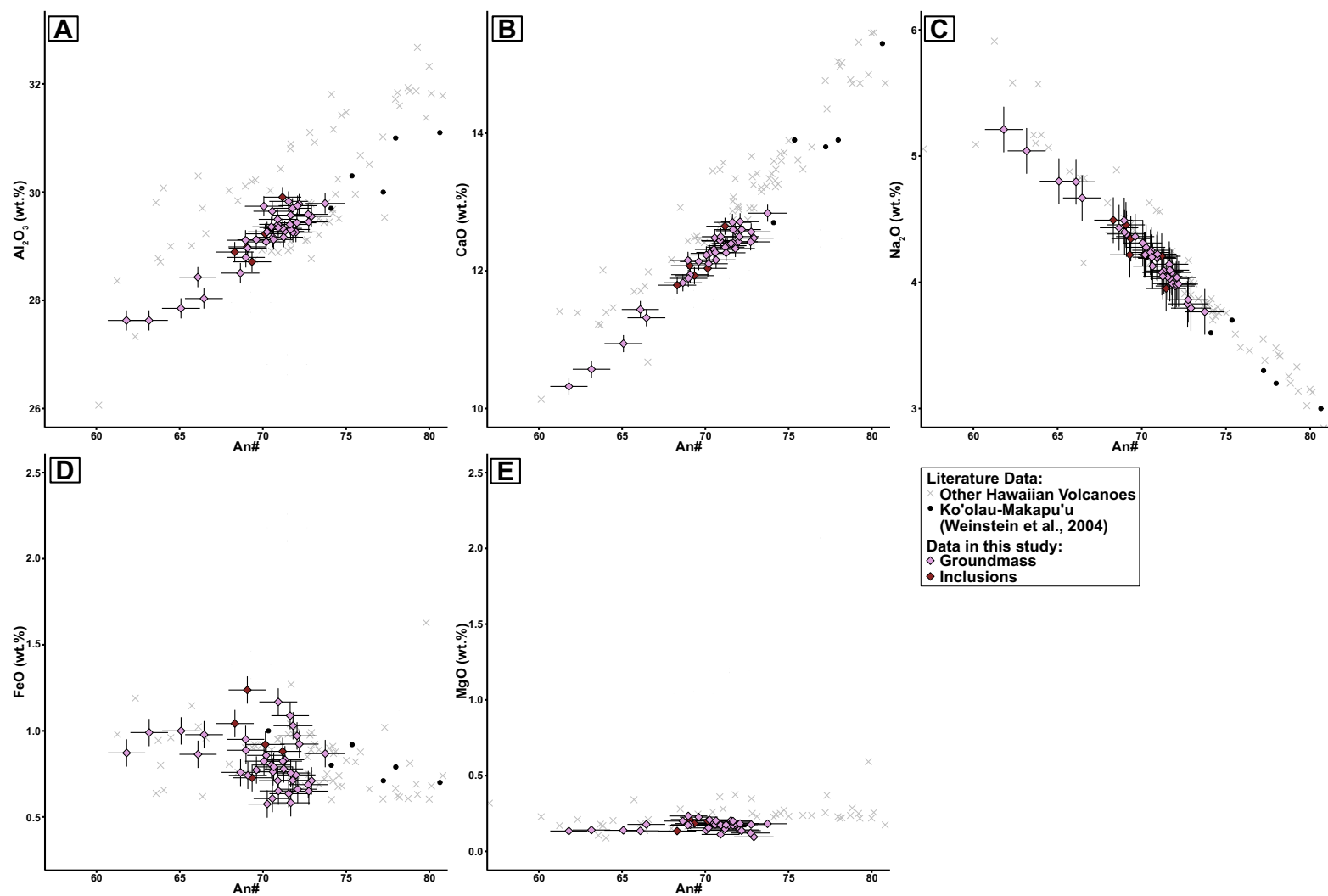


Figure 29: Plots of major, minor, and trace element compositions for groundmass and inclusion plagioclase within pyroxene phenocrysts in wt.% vs. anorthite content in mol.% collected via EPMA for both published data and data reported in this study. Other Hawaiian volcanoes include Kīlauea and Mauna Loa. Horizontal and vertical error bars represent calculated error reported in Supplementary Information A, Table 4.

PYX015 also shows much more complex zoning with multiple patches of higher Al_2O_3 wt.%, and Cr_2O_3 wt.% compositions, which is also evident in the BSE image (Figure 31). Both orthopyroxene phenocrysts have rims of clinopyroxene, as denoted by lower SiO_2 wt.% and higher MgO wt.% and CaO wt.%, as well as brighter color in BSE (Figure 30 and 31). PYX009 shows more defined, thicker, clinopyroxene rim compared to PYX015. In both cases, the clinopyroxene rims are epitactic. PYX009 shows plagioclase feldspar inclusions oriented parallel to orthopyroxene crystal faces, distinguished by higher Al_2O_3 wt.%, Na_2O_3 wt.%, and CaO wt.% (Figure 30). These feldspar inclusions are absent in PYX015 (Figure 31) but are common in other orthopyroxene phenocrysts in sample KOOB-5.

OLV006 displays an olivine macrocryst encased by a rim of orthopyroxene (Figure 32). The olivine macrocryst displays a small rim of alteration between the macrocryst and orthopyroxene reaction rim, likely of iddingsite, which is denoted by lower MgO wt.% and higher FeO wt.% (Figure 32). The olivine macrocryst shows complex, sawtooth resorption textures, and orthopyroxene (~4 wt.% CaO , as well as ~50 wt.% SiO_2 and ~25 wt.% MgO) encases the olivine macrocryst (Figure 32). The orthopyroxene rim continues the morphology of the olivine crystal face, rather than forming distinct crystals on the olivine-orthopyroxene margin. This morphology of pyroxene reaction rim on olivine macrocrysts is common among samples, however, distinct crystals also form on the margin of some olivine macrocrysts in other samples. Epitactic pyroxene rims that smoothly continue pre-existing crystal faces is most common in KOOB-5. The orthopyroxene rim has intergrown clinopyroxene zones shown by areas with relatively low FeO wt.% and high CaO wt.%, displaying up to ~18 wt.% CaO (Figure 32). It is common for samples to show multiphase reaction rims of orthopyroxene and clinopyroxene on olivine macrocrysts, although most rims are low-Ca clinopyroxene (Figure 22).

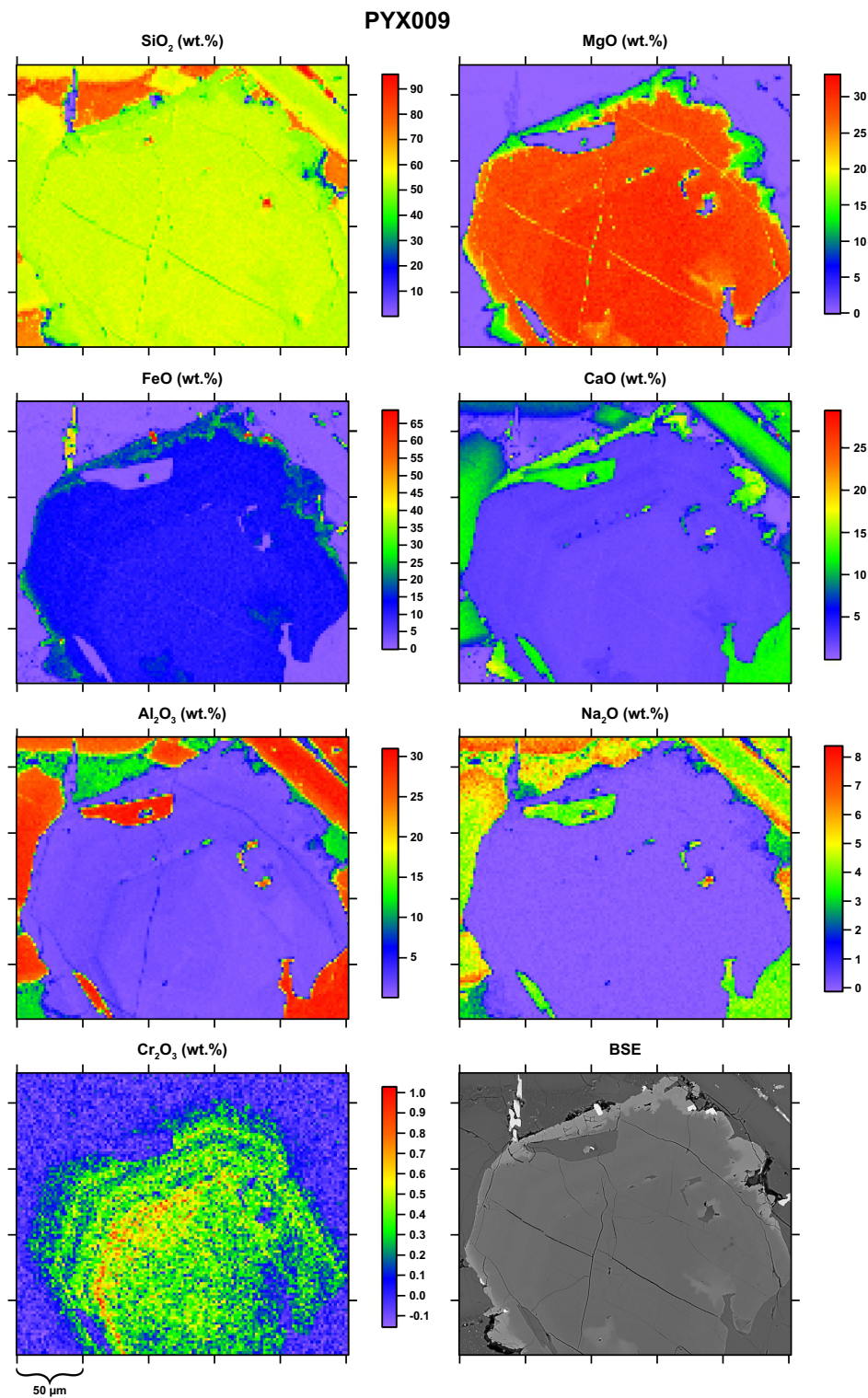


Figure 30: SiO₂, MgO, FeO, CaO, Al₂O₃, Na₂O, and Cr₂O₃ EPMA maps and backscatter electron image showing chemical heterogeneity of an orthopyroxene phenocryst from sample KOOB-5.

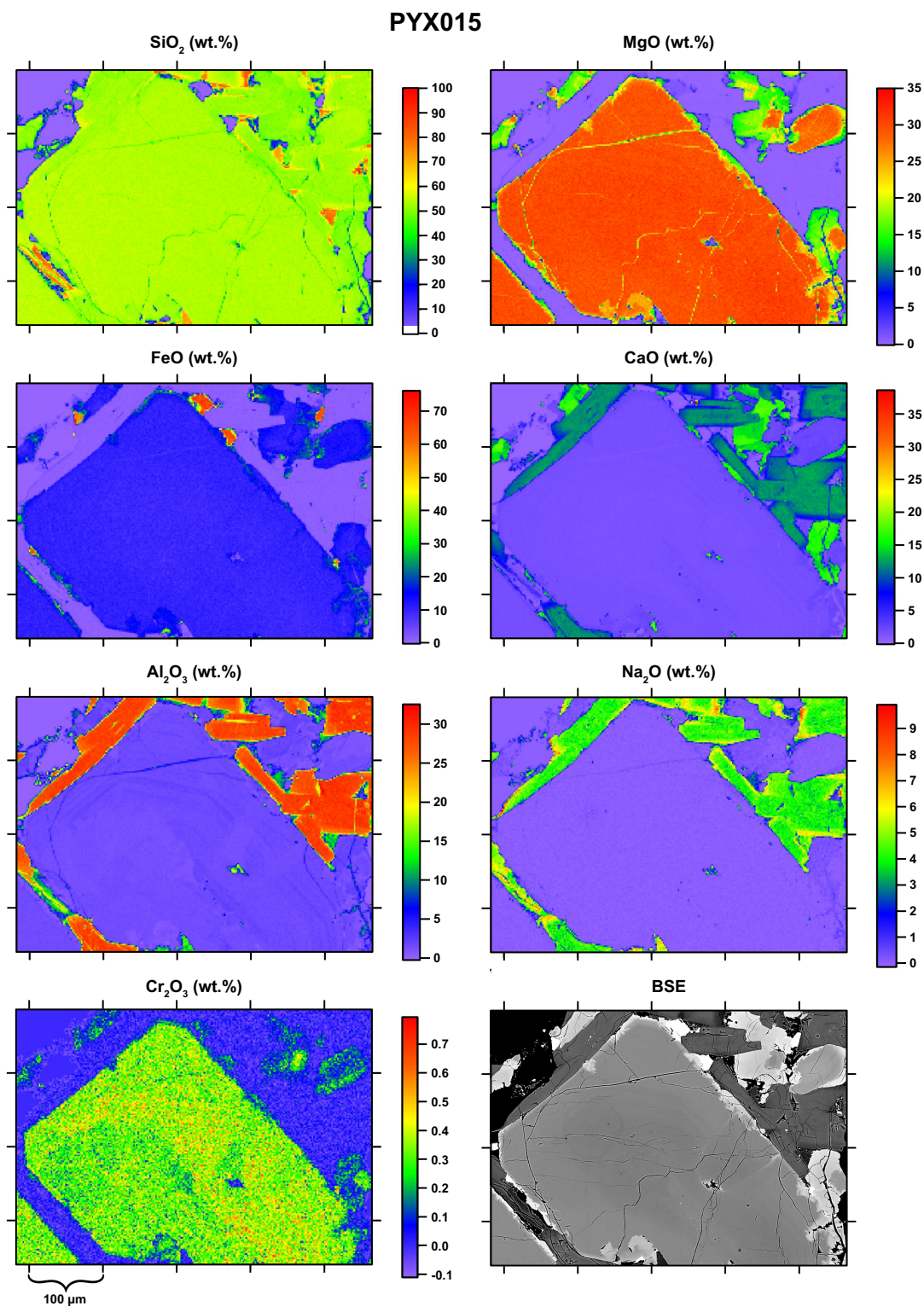


Figure 31: SiO₂, MgO, FeO, CaO, Al₂O₃, Na₂O, and Cr₂O₃ EPMA maps and backscatter electron image showing chemical heterogeneity of an orthopyroxene phenocryst from sample KOOb-5.

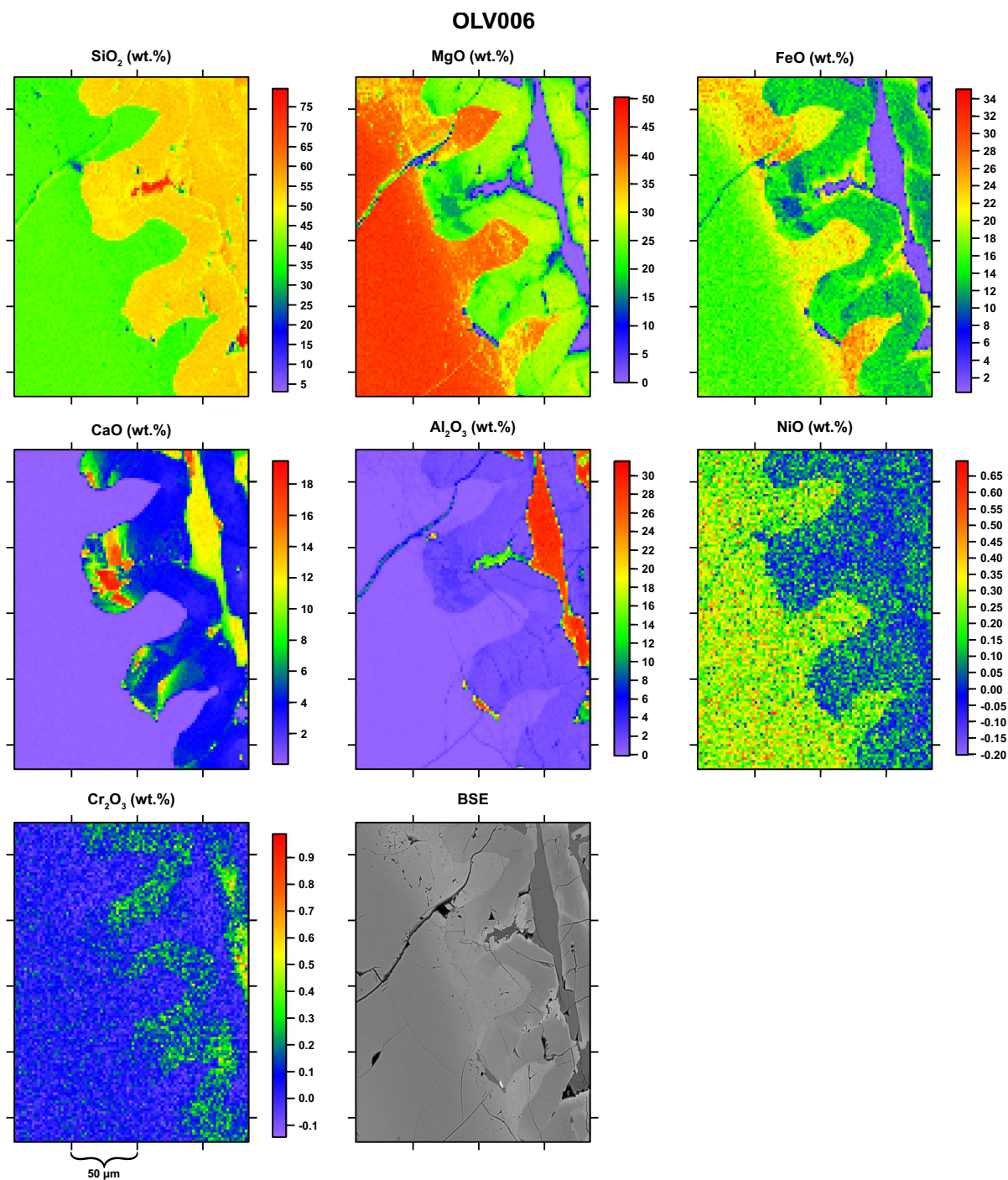


Figure 32: SiO₂, MgO, FeO, CaO, Al₂O₃, NiO, and Cr₂O₃ EPMA maps and backscattered electron image showing chemical heterogeneity of an olivine macrocryst with a pyroxene reaction rim from sample KOOB-5.

3.5 Thermometry: Tests for Equilibrium

3.5.1 Orthopyroxene

For orthopyroxene thermometry, *Thermobar* (Wieser et al., 2022) orthopyroxene-melt matching was used with a fixed K_d of 0.29 and K_d error of ± 0.06 (Putirka et al., 2008). Of the 60 orthopyroxene phenocrysts analyzed, 37 are in equilibrium with their whole-rock compositions (Figure 33A). Of the 28 orthopyroxene groundmass crystals analyzed, 13 are in equilibrium with their whole-rock compositions. Only one reaction rim and inclusion was in equilibrium.

There is no correlation between samples with orthopyroxene in equilibrium with their whole-rock compositions and stratigraphic order. Overall, there were no samples where all analyzed phenocryst and groundmass orthopyroxenes were in equilibrium with the whole-rock compositions. Crystallization temperatures for all orthopyroxenes in equilibrium were calculated (see section 3.6).

3.5.2 Clinopyroxene

For clinopyroxene thermometry, a K_d of 0.27 ± 0.03 was used to test for equilibrium with whole-rock compositions (Putirka, 2008). Of the 5 clinopyroxene antecrysts analyzed, 3 are in equilibrium with their whole-rock compositions. Of the 87 clinopyroxene groundmass analyzed and 98 clinopyroxene reaction rims analyzed, only 3 groundmass crystals and 1 reaction rim crystal is found to be in equilibrium with their whole-rock composition (Figure 33B). Only low-Ca clinopyroxenes are found to be in equilibrium with their whole-rock, with $Wo < 8$ mol%. Based on the small number of clinopyroxene found to be in equilibrium, clinopyroxene-liquid thermometry was not calculated.

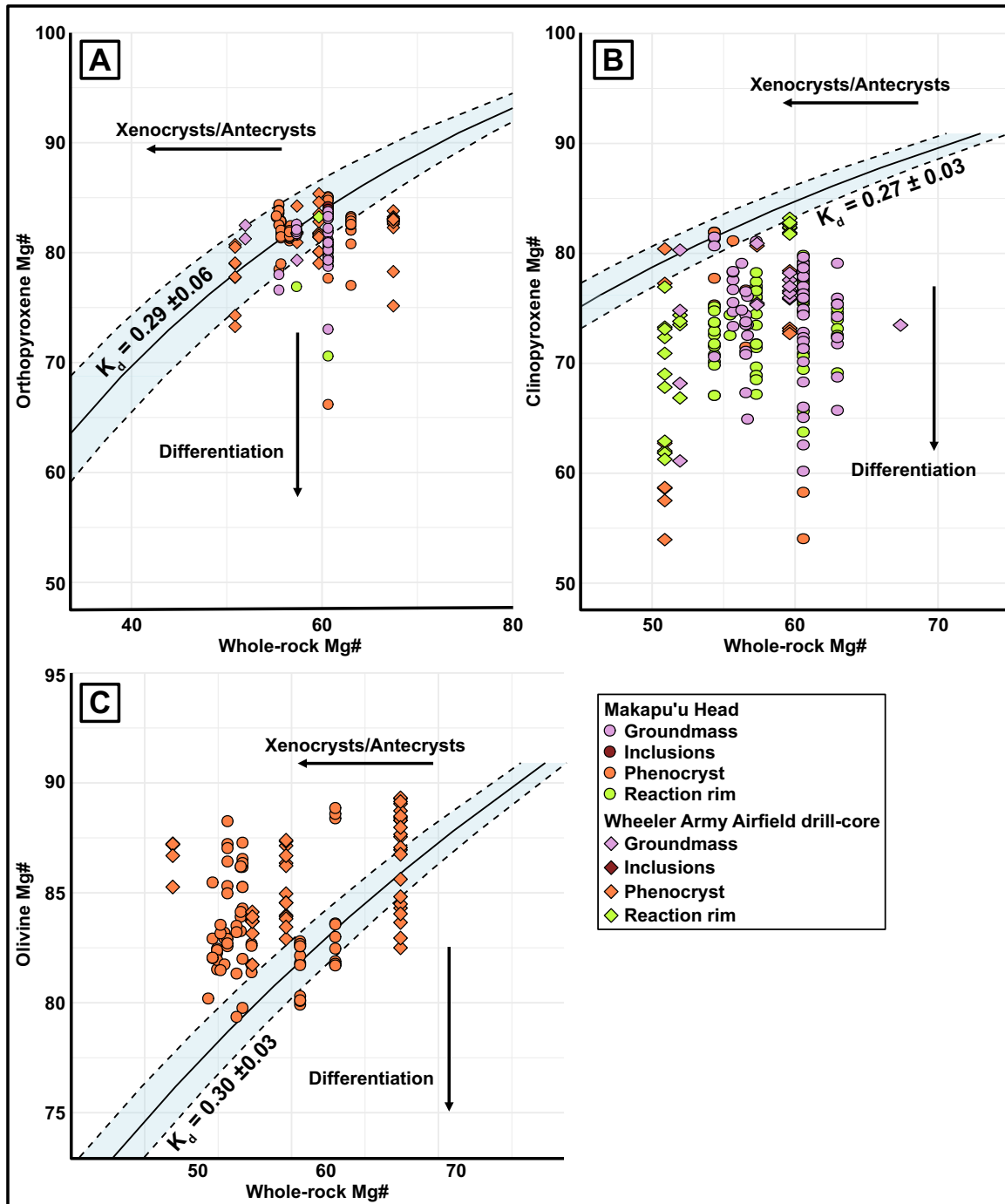


Figure 33: Rhodes diagrams of mineral Mg# vs. liquid, or whole-rock Mg# for A) orthopyroxene, B) clinopyroxene, and C) olivine macrocrysts measured in this study from Makapu'u Head and Wheeler Army Airfield drill-core. Arrows indicate interpretation of crystals which deviate from equilibrium compositions, where high crystal Mg# for a given whole-rock Mg# are xenocrysts or antecrysts, and low crystal Mg# for a given whole-rock Mg# are crystals formed by differentiation.

3.5.3 Olivine

For olivine thermometry, a K_d of 0.30 ± 0.03 was used to test for equilibrium with whole-rock compositions (Roeder and Emslie, 1970). Of the 151 olivine macrocrysts and antecrysts analyzed, 18 are in equilibrium with their whole-rock compositions (Figure 33C). All samples with olivine in equilibrium contain other olivine macrocrysts and antecrysts that were not in equilibrium with their whole-rock compositions. Also, the morphologies of the macrocrysts found to be in equilibrium are quite diverse from large, subhedral grains (Group 1), largely resorbed grains (Group 2), small grains (Group 5), and glomerocrysts (Group 6). No skeletal olivine (Group 3) or elongated olivine (Group 4) morphologies were in equilibrium with their whole-rock compositions. Based on the small number of olivine found to be in equilibrium with the whole-rock and extensive petrologic evidence of disequilibrium (e.g., highly resorbed grains) and xeno- or autocrystic grains (e.g. glomerocrysts), we can hypothesize that these crystals are in equilibrium with their whole-rock chemistry by coincidence rather than being true phenocrysts crystallized from a magma of the composition of the whole-rock. For a more robust olivine thermometry dataset, we analyze olivine with their spinel inclusions for olivine-spinel aluminum exchange thermometry, on the basis that the spinel inclusions are in equilibrium with their olivine host. This offers a reliable source for olivine thermometry, which does not rely on equilibrium with whole-rock compositions.

3.6 Thermometry Calculations

Temperatures calculated from Eq.28a (Putirka, 2008) for orthopyroxene-liquid thermometry are summarized in Supplementary Information A, Table 6. Orthopyroxene-liquid calculations yield temperatures ranging from $1165 \pm 41^\circ\text{C}$ – $1232 \pm 41^\circ\text{C}$ for all populations. Phenocryst record a larger range of crystallization temperatures, while groundmass and inclusions show a tighter cluster of crystallization temperatures (Figure 34).

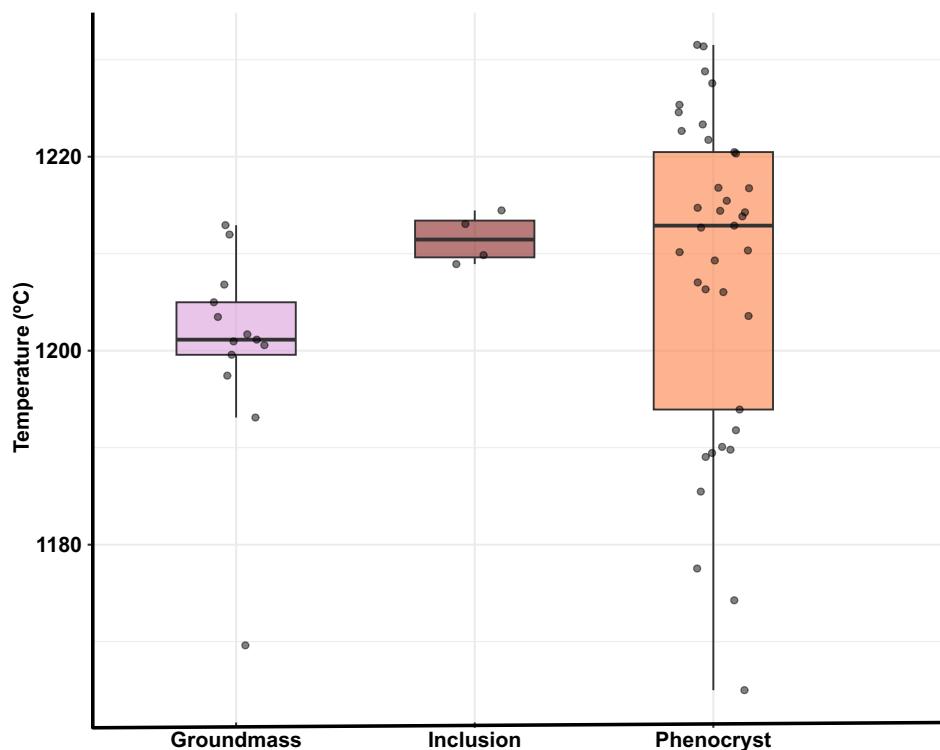


Figure 34: Box plot showing distribution of calculated temperatures (°C) for orthopyroxenes in Makapu‘u Head and Wheeler Army Airfield drill-core samples. Calculated temperature (°C) for the one reaction rim in equilibrium is not shown.

Olivine-spinel aluminum exchange thermometry temperatures for Makapu‘u Head and Wheeler Army Airfield drill-core are summarized in Supplementary Information A, Table 5. Overall, olivine temperatures range from $998 \pm 34.2^{\circ}\text{C}$ – $1264 \pm 34.2^{\circ}\text{C}$ with an average of $1058 \pm 34.2^{\circ}\text{C}$. Wheeler Army Airfield drill-core samples WH-636, WH-541, and WH-489 display average temperatures of 1128°C , 1036°C , and 1022°C , respectively, decreasing in temperature with time. Makapu‘u Head samples KOOB-9B and KOOB-12B display average temperatures of 1037°C and 1051°C . Makapu‘u Head temperatures seem to increase with time, although average temperatures for KOOB-9B and KOOB-12B are within error established by Zhang et al. (2023). Orthopyroxene temperatures seem to vary through time. Makapu‘u Head displays cyclic higher to lower temperature pulses (Figure 35). Wheeler Army Airfield seems to follow the same trend, although with lower sample resolution it is impossible to be certain (Figure 35).

Generally, orthopyroxene temperatures are higher than olivine temperatures (Figure 35). Anomalous low olivine crystallization temperatures yielded by OSAT is likely the result of sub-solidus Cr re-equilibration, in which slow cooling of the lava allowed time for Cr to diffuse in olivine before cooling below the closure temperature (Ito & Ganguly, 2006; Jollands et al., 2018; Zhang et al., 2023). We therefore interpret that crystallization of olivine and spinel inclusions occurred above the Cr diffusive re-equilibration closure temperature, and slow cooling to reach the closure temperature effectively re-set the temperatures calculated from OSAT to abnormally low temperatures. Although OSAT temperatures are likely not representative of the true olivine crystallization temperature, the relative OSAT temperatures between samples can be used to interrogate any trends in oscillating temperature, and thus any magma rejuvenation events recorded by relatively higher temperature.

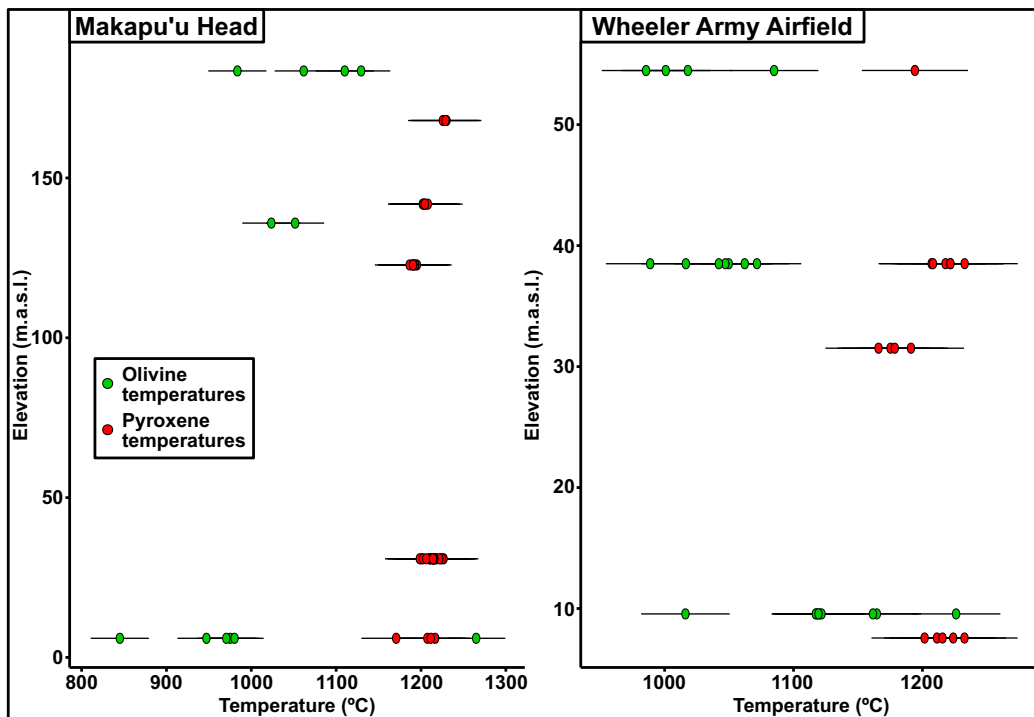


Figure 35: Calculated orthopyroxene-liquid temperatures (°C) and olivine-spinel aluminum exchange temperatures (°C) in stratigraphic order for Makapu'u Head (left) and Wheeler Army Airfield drill-core (right).

CHAPTER 4 – DISCUSSION

Sr-Pb-Nd-Hf isotopic studies have demonstrated that geochemical heterogeneity exists within the Hawaiian mantle plume, and basalt compositions can be explained by mixing of multiple isotopic endmembers (Hauri, 2002; Tanaka et al., 2002; Weis et al., 2020; Williamson et al., 2025). Enriched Loa volcanoes, and Ko‘olau Volcano specifically, has a unique mantle source relative to other Hawaiian volcanoes, based on statistically distinct $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{208}\text{Pb}/^{206}\text{Pb}$ enrichment and $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{176}\text{Hf}/^{177}\text{Hf}$ depletion (Frey et al., 2016; Huang et al., 2005; Huang & Frey, 2005; Tanaka et al., 2008; Williamson et al., 2025). In addition to isotopic (Armstrong, 2022; Fekiacova et al., 2007; Weis et al., 2020; Williamson et al., 2025) and whole-rock geochemistry differences (Frey et al., 1994; Haskins & Garcia, 2004; Jackson et al., 2012; Tanaka et al., 2002), this study shows multiple lines of evidence that Ko‘olau-Makapu‘u lavas experienced strong chemical disequilibrium and magma mixing that is unusual for a Hawaiian shield volcano. The subsections that follow outline that evidence, including mineral scale textural and chemical, whole-rock isotopic, and thermometric evidence. The following discussion will also provide a theoretical model for the petrogenesis of Ko‘olau-Makapu‘u basalts.

4.1 Textural Evidence for Magma Mixing

The presence of magma mixing in Ko‘olau lavas studied here is supported by olivine, plagioclase, and pyroxene that all show petrologic textures indicative of chemical disequilibrium with their carrier melt. Olivine by far shows the strongest disequilibrium textures, with embayments and rounding of crystal edges that occurs when pre-existing olivine begin melting. Olivine also displays pyroxene reaction rims, providing further support for chemical disequilibrium between the olivine and the host liquid. In some cases, these pyroxene reaction

rims are crystalline, while others show evidence of simultaneous resorption and reaction along the crystal grain boundary (e.g. OLV006; Figure 32), evidence of interaction with a more siliceous melt (Coombs & Gardner, 2004). Pyroxene and plagioclase show resorption evidence of disequilibrium, and, in the case of pyroxene, epitactic overgrowth rims, although to a lesser degree.

It is not uncommon for Hawaiian lavas to carry crystal cargo from the magma storage cumulate mush to the surface and for those crystal cargos to show mild evidence of chemical disequilibrium. In fact, olivine is commonly used as a record of magma mixing events and chemical disequilibrium in Hawaiian lavas (De Maisonnette et al., 2016; Kahl et al., 2023; Ruth et al., 2018; Shea et al., 2019; Shea et al., 2015b). Many of these studies show Kea- and Loa-type lavas that display resorption textures and gradients of chemistry from core to rim that are used for diffusion chronometry studies (Costa et al., 2008, 2020; Dohmen & Chakraborty, 2007; Lynn et al., 2017a; Lynn et al., 2024b). Thus, chemical disequilibrium has been documented among Hawaiian volcanoes, and magma rejuvenation as a magmatic process in Hawaiian volcanoes is well accepted. What is different about Ko‘olau Volcano, however, is that the magma that is rejuvenating the system towards the end of the shield stage is enriched in SiO_2 and depleted in CaO and TiO_2 relative to other Hawaiian parental melts (Jackson et al., 2012). The injection of such melt, unique to the Hawaiian system, results in drastically greater disequilibrium and textures unobserved at other Hawaiian volcanoes.

4.2 Mineral Scale Chemical Evidence for Magma Mixing

Previous major and trace element studies have shown that whole-rock compositions at Ko‘olau-Makapu‘u cannot be resolved by fractional crystallization (Blichert-Toft et al., 1999; Hauri, 1996; Lassiter & Hauri, 1998). Linear arrays of whole-rock compositions on major

element variation diagrams are usually an indicator of fractional crystallization controlling whole-rock compositions (Moore & Evans, 1967; Putirka, 2005; Vogel et al., 2008). For Ko‘olau samples studied here, whole-rock compositions do not plot in a linear array on major element variation diagrams, nor do compositions form a trend that points to any mineral composition measured in the rock (Figure 36). Analysis of mineral chemistry in this study reveals the same conclusion. Olivine and pyroxene have a large range of major element compositions, which is likely a result of mixing with multiple magma compositions rather than fractional crystallization alone.

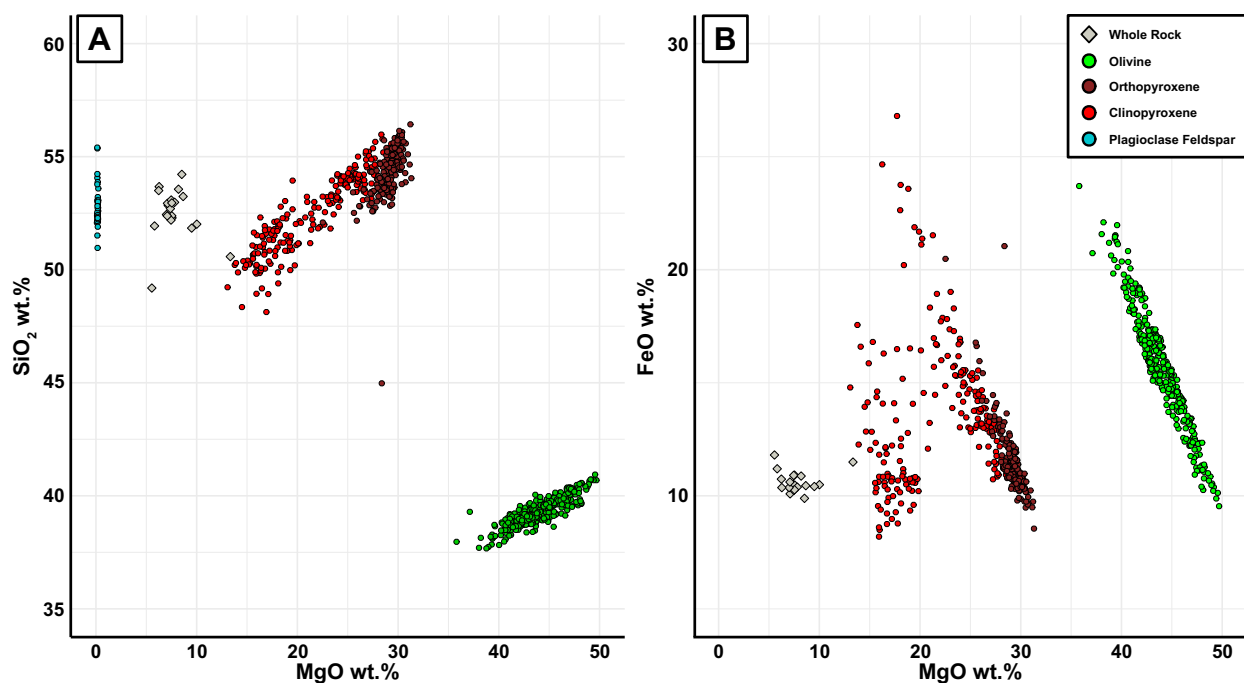


Figure 36: MgO variant plots of major elements SiO₂ and FeO in wt.% for whole-rock geochemistry and olivine, pyroxene, and plagioclase EPMA data for Makapu'u Head and Wheeler Army Airfield samples.

Transects from core to rim of orthopyroxene phenocrysts reveal complex zoning patterns (Figure 15), evidence of magma mixing rather than crystallization in a closed-system evolving melt (Winslow et al., 2025). This is also depicted in pyroxene chemical maps, which display

complex zoning in Cr_2O_3 , Al_2O_3 , and CaO (Figure 30 and 31). Some orthopyroxene phenocrysts show evidence of at least three magma mixing events, as depicted by three peaks of high $\text{Mg\#}$ in each core-rim transect (Figure 15) and three zones of higher Cr_2O_3 , Al_2O_3 , and CaO in one pyroxene chemical map (Figure 30).

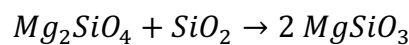
Olivine is dominantly normally zoned and does not show complex zoning from core to rim (Figure 15). However, olivine are dominantly interpreted as antecrysts based on the presence of resorption textures and reaction rims; they were likely entrained from crystalline mush in the shallow crustal reservoir, where long storage at elevated temperatures would have resulted in Fe-Mg equilibrium because the rate of diffusion of Fe-Mg diffusion in olivine is relatively fast, especially relative to Fe-Mg interdiffusion in pyroxene (Dohmen et al., 2016). Thus, the core to rim in the olivine is likely recording the steady-state fractional crystallization of the shallow crustal reservoir prior to injection of a new composition, which is recorded by the resorption textures and pyroxene reaction rims.

4.3 The Pyroxene Paradigm: A Unique Mineral Assemblage

Shield-stage Hawaiian lavas generally contain similar mineral assemblages. Early petrographic studies describe Kea- and Loa-trend shield-stage basalts from Mauna Loa, Mauna Kea, Kīlauea, Kohala, Hualālai, Ni‘iahu, Moloka‘i, and Haleakalā that are composed of dominantly olivine with minor plagioclase and augite phenocrysts within a groundmass consisting of dominantly plagioclase with pigeonite, augite, $\pm$ olivine (Macdonald, 1947a, 1947b, 1949; Macdonald & Powers, 1946). More recent petrographic studies of Mauna Loa and Kīlauea describe a similar mineral assemblage with the addition of orthopyroxene phenocrysts in some Mauna Loa historic eruptions (Baker et al., 1996; Couperthwaite et al., 2022; M. Garcia et al., 1989; Garcia, 1996; Kahl et al., 2023; Wilkinson & Hensel, 1988; Winslow et al., 2025).

Contrary to this simple basalt mineral assemblage of other Hawaiian volcanos, Ko‘olau-Makapu‘u lavas have a greater abundance of pyroxene, both orthopyroxene and clinopyroxene, that occurs as phenocrysts, in the groundmass, and as reaction rims on olivine or pyroxene. Where pyroxene phenocrysts are present, Ko‘olau-Makapu‘u lavas are dominated by orthopyroxene with absent or rare clinopyroxene (Frey et al., 1994; Muir & Long, 1965; Tanaka et al., 2002). The same is true for lavas analyzed in this study, which contain 60 orthopyroxene phenocrysts and 2 clinopyroxene antecrysts in the sample suite. Furthermore, Ko‘olau-Makapu‘u lavas contain orthopyroxene, pigeonite, and augite as groundmass and reaction rims, which is unique compared to Mauna Loa shield-stage basalts (Baker et al., 1996; Garcia, 1996; Kahl et al., 2023; Macdonald, 1949; Winslow et al., 2025). It is not uncommon for olivine and pyroxene phenocrysts in Hawaiian lavas to have overgrowths of pigeonite and/or augite, however, orthopyroxene reaction rims have not yet been documented in any Loa- or Kea- trend Hawaiian volcano (Couperthwaite et al., 2022; Kahl et al., 2023; Macdonald, 1949; Moore & Evans, 1967; Yang et al., 1999).

Experiments show that orthopyroxene reaction rims form on olivine when the olivine reacts with a high-silica melt (Coombs & Gardner, 2004; Grove & Juster, 1989; Tsuchiyama, 1986). This is a peritectic reaction, in which a solid and liquid phase assemblage react to form a new solid and liquid phase assemblage. The peritectic reaction recorded here is as follows, where solid olivine reacts with a liquid silica-rich melt to form solid orthopyroxene:



SiO₂-rich melts associated with arc systems commonly display orthopyroxene reaction rims on olivine xenocrysts (Kamenetsky et al., 2006; Streck et al., 2007), however this sort of reaction has not been documented in Hawai‘i before. This peritectic reaction in Ko‘olau-

Makapu‘u samples is consistent with the basaltic andesite composition of Ko‘olau-Makapu‘u rocks, which is higher silica relative to other Hawaiian volcanoes that erupt mostly basalts (Jackson et al., 2012; Armstrong, 2022; Williamson et al., 2025).

Basaltic andesites have rarely been documented at other Hawaiian volcanoes. A famous example is the basaltic andesite erupted during the initial phase of the lower east rift zone eruption of Kīlauea volcano in 2018. Evolved compositions of early lavas were interpreted as a fractionated dike that had been emplaced into the rift zone decades before and evolved to basaltic andesite while isolated from interaction with primitive, basaltic magma (Gansecki et al., 2019). However, basaltic andesite erupted for a short time because only a small volume of fractionated magma formed in the rift zone. Ko‘olau is fundamentally different, in that all lavas erupted to form the Ko‘olau-Makapu‘u late shield stage cap are basaltic andesite in composition, suggesting a much larger source of high silica than small-volume rift emplaced dikes.

Systemic higher silica in Ko‘olau lavas have not been adequately explained by fractional crystallization or shallow crustal processes like assimilation (Hauri, 1996; Lassiter and Hauri, 1998; Blichert-Toft et al., 1999). Instead, it is thought the high silica originates from mantle source lithologic heterogeneity (pyroxenite, eclogite) that provides higher silica to the generated melt than an equivalent volume of peridotite (Jackson et al., 2012; Lambart et al., 2012; Pertermann & Hirschmann, 2003). Although identification of the mantle source for Ko‘olau-Makapu‘u lavas is outside of the scope of this study, the higher abundance of orthopyroxene and reaction rims of orthopyroxene around olivine macrocrysts in our samples provide petrologic evidence of chemical disequilibrium between multiple batches of melt. Based on these previous whole-rock and isotope studies, proposed mantle sources for Enriched Loa volcanics, and experimental petrology studies, the high abundance of orthopyroxene in Ko‘olau-Makapu‘u

lavas can be explained by the reaction between a high-silica eclogitic or pyroxenite melt from the mantle and dunite, wehrlite, or gabbro cumulate mush in the shallow, sub-caldera magma reservoir.

Ko‘olau-Makapu‘u samples exhibit pigeonite and augite as a groundmass phase and reaction rims on olivine macrocrysts, as well as epitactic overgrowth on orthopyroxene phenocrysts. This is somewhat contradictory to a higher-silica melt reacting with a peridotite mush, which typically promotes the crystallization of orthopyroxene, not higher-Ca pyroxenes (Coombs and Gardner, 2004). The presence of pigeonite and augite as groundmass and rim phases is quite common in Hawaiian volcanoes, and is interpreted as either late-stage, rapid crystallization under lower pressures in a melt that underwent simple fractional crystallization (Couperthwaite et al., 2022; Nicholls & Stout, 1997; Poldervaart & Hess, 1951) or evidence of disequilibrium from injection of a more primitive, Ca-rich melt (Winslow et al., 2025). In fact, pigeonite rims on olivine phenocrysts at Mauna Loa have been interpreted as a post-emplacement texture caused by chemical disequilibrium during surficial lava flow, not from crystallizing at depth (Couperthwaite et al., 2022). Texturally, our Ko‘olau-Makapu‘u samples have evidence of rapid crystallization such as skeletal olivine macrocrysts and skeletal chromites in the groundmass, suggesting high degrees of undercooling in some lavas (Donaldson, 1976). The low CaO of Ko‘olau lavas rules out an injection of a Ca-rich melt. Thus, it is possible that the clinopyroxene and pigeonite phases in the groundmass and epitactic overgrowths on orthopyroxene phenocrysts are a result of low-pressure, rapid crystallization as the magma traverses to eruption.

4.4 Evidence for Cyclic Magma Rejuvenation of Makapu‘u Endmember

Further evidence of magma rejuvenation exists in the Pb-Sr-Hf-Nd isotopic ratios. Enriched Loa lavas are characterized by higher $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and lower $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ relative to other Loa- and Kea-trend Hawaiian volcanoes (Armstrong, 2022; Weis et al., 2020; Williamson et al., 2025). Using stratigraphic order as a proxy for time, there are cycles of isotopic composition variation where spikes in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ accompanied by depletions in $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ indicate the arrival of batches of magma with different isotopic compositions, here interpreted as Ko‘olau-Makapu‘u melt (Figure 5). Subsequent decreasing of $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and increasing of $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ likely indicate mixing and dilution in a larger reservoir before the next magma rejuvenation event.

There is ample evidence of chemical disequilibria on the physical (e.g. resorption) and chemical (e.g. orthopyroxene chemical zoning) scale. Specifically, there is evidence of a reaction between olivine and high-silica melt as indicated by orthopyroxene reaction rims (Tsuchiyama, 1986; Grove and Juster, 1989; Coombs and Gardner, 2004). The subsequent decrease in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and increase in $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ after an injection event likely represents dilution of the isotopic signature through the mixing and reaction of the Ko‘olau-Makapu‘u melt with the pre-existing dunite, wehrlite, or gabbro cumulate mush in the shallow, sub-caldera magma reservoir. It is also possible that assimilation of the Loa-type wall rock further dilutes the Ko‘olau-Makapu‘u isotopic signature, as has been documented at Kīlauea eruptions over the last 200 years (Garcia et al., 2007, 2025). There, assimilation of 3.5-12% of variably hydrothermally altered wall rock likely in the shallow magma reservoirs results in the variation of oxygen isotopic composition of erupted lavas (Garcia et al., 2008). Oxygen and

osmium isotopic compositions at West Maui are thought to result from assimilation of either oceanic crust as lavas transit from the mantle to the shallow edifice or wall rock to the shallow magma reservoir, that become more important towards the waning of the shield stage (Gaffney et al., 2005).

Reaction with the Loa-type cumulate mush or assimilation of Loa-type wall rock are both plausible because of partition coefficients of Pb, Sr, Hf, and Nd in olivine, pyroxene, and plagioclase. Olivine is not likely to contribute to a change in Pb-Sr-Nd-Hf isotopic signatures, because the partition coefficients of Pb, Sr, Nd, and Hf are 0.0001, 0.0001, 0.00004, and 0.001, respectively (White, 2017). Thus, olivine is not a primary carrier of these isotopes and the resorption of olivine will not affect isotopic compositions. Similarly, orthopyroxene is likely not contributing to diluting isotopic compositions ($K_d < 0.02$ for Pb, Sr, Nd, and Hf). Clinopyroxene and plagioclase, however, have relatively high partition coefficients for these elements. Resorption of clinopyroxene could be the contributing factor to changing Nd and Hf ($K_d = 0.28$ and 0.24 , respectively) and resorption of plagioclase is the likely contributing factor to changing Pb and Sr ($K_d = 0.75$ and 2.5 , respectively). It is likely that the fractionated Loa-type cumulate mush in shallow, sub-caldera magma reservoirs or Loa-type wall rock have clinopyroxene and plagioclase available to resorb and dilute the Ko‘olau-Makapu‘u isotopic signature through simple magma mixing.

Based on Pb-Sr-Hf-Nd isotopic ratios, there is evidence of at least three Ko‘olau-Makapu‘u rejuvenation events at Makapu‘u Head and Wheeler Army Airfield drill-core, characterized by the cyclic expression of higher $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ with lower $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ (Figure 5). Whether these expressions of the Ko‘olau-Makapu‘u isotopic signature at the two localities are linked to the same rejuvenation event is unclear given their

locations on opposite sides of the caldera. Regional flow dip directions and detailed mapping to link the two localities together would be needed to temporally correlate flows at Makapu‘u Head and Wheeler Army Airfield drill-core, along with techniques like paleomagnetic analysis of basalts on each flank of the volcano. Nonetheless, the two localities both demonstrate cyclic arrival of the Ko‘olau-Makapu‘u isotopic signature.

The same cyclic behavior is observed through the stratigraphic sequence for olivine Fo, pyroxene Mg#, and calculated olivine-spinel aluminum exchange thermometry and orthopyroxene-liquid thermometry temperatures (Figure 37). An increase in olivine Fo, pyroxene Mg#, and temperature indicates injection of a more primitive magma, and subsequent lowering of these values indicate evolution and mixing of the system (De Maisonneuve et al., 2016; Ruprecht & Welsch, 2023; Sakuyama, 1979). At Makapu‘u Head, peaks of high Fo (Figure 37A) and high Mg# (Figure 37B) correlate with the peak expression of the Ko‘olau-Makapu‘u isotopic signature at the same depths (Figure 37A-D). This suggests that the rejuvenating, high MgO parental melt injected into the shallow reservoir carried the Enriched Loa geochemical composition and rejuvenated the system in a cyclic manner. This trend roughly correlates with orthopyroxene-liquid temperatures, which experience peaks of higher temperatures at the same depths as the magma rejuvenation events identified with isotopic composition and olivine Fo (Figure 37D). The cyclic trend cannot be resolved within olivine-spinel aluminum exchange thermometry because sample resolution is too low (Figure 37C). At the base of the Wheeler Army Airfield drill-core, however, the same correlation can be resolved between isotopic signatures (Figure 5), olivine Fo%, pyroxene Mg#, OSAT temperatures, and orthopyroxene-liquid temperatures (Figure 37E-H).

Cyclic high Fo to low Fo olivine is somewhat contradictory to the antecrystic olivine interpreted in Ko‘olau-Makapu‘u basalts. If the olivine pre-exists in the Loa-type cumulate mush, Fo content should not record injection of primitive magma. However, it is likely that the initial pulse of Ko‘olau-Makapu‘u lavas preferentially carried high-Fo olivine from the deep magma storage cumulate mush to eruption, thus explaining high-Fo olivine in the samples with high temperature and peak Ko‘olau-Makapu‘u isotopic signatures. In the case of Kīlauea, the deep magma reservoir contains high-Fo olivine while the shallow magma reservoir contains fractionated, low Fo olivine, and it is common for lavas to carry pre-existing high-Fo olivine to the surface (Wieser et al., 2020a). Subsequent low-Fo olivine recorded in diluted Ko‘olau-Makapu‘u samples likely reflect continued mixing and reaction, where high Fo olivine is completely resorbed. Thus, cyclic olivine Fo is not likely recording crystallization from cyclic pulses of primitive magma, but instead, sampling of olivine from the Loa-type cumulate mush and subsequent dissolving of olivine during mixing.

Samples KOOb-15, KOOb-8, and KOOb-6 represent the peak expression of the Ko‘olau-Makapu‘u isotopic signature at Makapu‘u Head, and WH-182 (not analyzed in this study), WH-489, and WH-642 represent the peak expression of the Ko‘olau-Makapu‘u isotopic signature at Wheeler Army Airfield drill-core. There is no correlation between groundmass and macrocryst textures or mineral assemblage (e.g. modal abundance of orthopyroxene) within the samples that display the peak expression of the Ko‘olau-Makapu‘u isotopic signature. Nonetheless, the cyclic isotopic compositions, olivine Fo%, pyroxene Mg#, and temperatures along with strong petrologic evidence of magma rejuvenation and chemical disequilibrium suggests cyclic rejuvenation of the Ko‘olau-Makapu‘u chemical endmember.

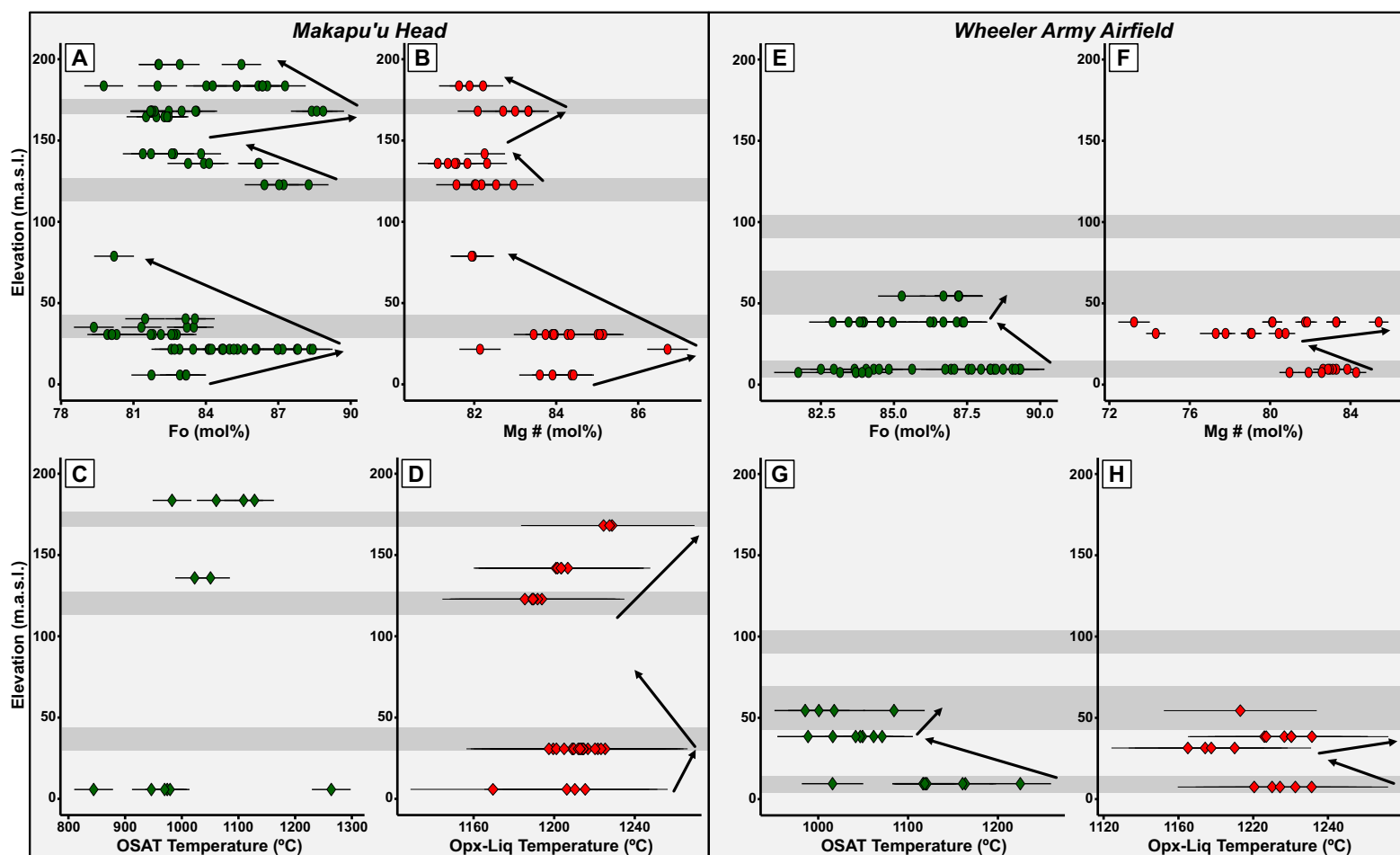


Figure 37: Plots of olivine and pyroxene compositions and temperatures as a function of stratigraphic order, showing A) olivine Fo at Makapu 'u Head, B) pyroxene Mg# at Makapu'u Head, C)olivine Fo at WAA, D) pyroxene Mg# at WAA, E) olivine-spinel aluminum exchange thermometry temperatures at Makapu 'u Head, F) orthopyroxene-liquid temperatures at Makapu 'u Head, G) olivine-spinel aluminum exchange thermometry temperatures at WAA, and H) orthopyroxene-liquid temperatures at WAA. Arrows point to cyclic magma rejuvenation (high Fo%, Mg#, °C) and subsequent evolving of magma to lower Fo%, Mg#, and °C, and highlighted sections indicate Ko'olau-Makapu'u rejuvenation events interpreted from isotopic compositions. .

4.5 A Note on High Nickel in Olivine

EPMA analyses display mineral-scale chemical heterogeneity between Ko‘olau-Makapu‘u lavas and lavas from other Kea- and Loa-type volcanoes. A vast majority of EPMA data on Hawaiian lavas are for olivine, which provides a unique opportunity to statistically compare elemental compositions of olivine in Enriched Loa lavas to those in other Kea- and Loa-trend lavas. Olivine from Ko‘olau-Makapu‘u are statistically higher in NiO and lower in MnO and CaO. This is consistent with recent models suggesting an eclogite or pyroxenite-derived melt as the source of Ko‘olau-Makapu‘u geochemistry (Hauri, 1996; Sobolev et al., 2005, 2007). Sobolev et al. (2005, 2007) argued that the high-NiO content in olivine and high-SiO₂ whole-rock compositions are inconsistent with current Hawaiian melting models (e.g., that Hawaiian melts are derived from high degree melts of a harzburgite or garnet lherzolite).

Most models of harzburgite or garnet lherzolite melting can explain the high SiO₂ whole-rock compositions but fail to explain the high NiO in olivine. Sobolev et al. argues that this enigma can be resolved by a high-SiO₂ melt from an eclogite source reacting with mantle peridotite to produce an olivine-free pyroxenite that later melts to form parental Hawaiian melts that, once diluted with melt derived from peridotite, result in volcanoes with more or less of an Enriched Loa geochemical composition (Sobolev et al., 2005, 2007). The secondary pyroxenite would produce a melt unusually high in Ni, since olivine is not present to buffer the Ni composition of the melt to low concentrations.

This model requires that the Ko‘olau-Makapu‘u melt produces olivine with high Ni. However, most olivine compositions in this study have similar NiO concentrations at a given forsterite composition to other Loa-type volcanoes (Figure 25). Furthermore, olivine in Ko‘olau-Makapu‘u lavas are heavily resorbed, have pyroxene reaction rims, and are not in equilibrium

with their host rock. This evidence supports that olivine analyzed in Ko‘olau-Makapu‘u samples are antecrystic and picked up from the Loa-type cumulate mush in the magma storage reservoir(s). Nonetheless, Ko‘olau-Makapu‘u olivine have CaO wt.% > 0.1% (range from ~0.1 - 0.3%) and are non-mantle olivine (Thompson & Gibson, 2000; Wieser et al., 2020a) and therefore are not a good indicator of mantle compositions. Furthermore, source lithology is not the only potential cause of high Ni in olivine. For example, experiments have shown that the partition coefficient of Ni in olivine is sensitive to the silica content of the melt, with D_{Ni} (ol-melt) increasing with increasing melt SiO₂ (Wang & Gaetani, 2008). Ni in olivine can be changed by fractional crystallization, magma mixing, or diffusive re-equilibration of Fe-Mg, Mn, and Ni, which can overprint any chemical characteristics acquired during crystal growth (Lynn et al., 2017b). On the whole, with the weak statistical significance of high Ni olivine of Koolau lavas, the fact that the partition coefficient of Ni in olivine may be higher from the silicious composition of recharge melts, and variable amounts of magma mixing all suggest that the control of Ko‘olau olivine Ni compositions is more complex and requires involvement of more processes than simply source lithologic heterogeneity.

4.6 Petrologic Model for the Petrogenesis of Ko‘olau-Makapu‘u Basalts

Ko‘olau-Makapu‘u lavas at Makapu‘u Head and in the Wheeler Army Airfield drill-core provide a unique opportunity to characterize the dying of a Hawaiian shield volcano with a geologically constrained stratigraphic sequence of samples. Petrography and EPMA analyses reveal that chemical disequilibria and magma mixing are important processes in the petrogenesis of Ko‘olau-Makapu‘u basalts. This is further supported by at least three magma rejuvenation events recorded in orthopyroxene Mg#, Al₂O₃, Cr₂O₃, and CaO zoning, cyclic Ko‘olau-Makapu‘u isotopic signatures, and cyclic olivine Fo and pyroxene Mg#. The presence of

orthopyroxene indicates mixing with a high-silica melt, consistent with whole-rock geochemistry for Ko‘olau-Makapu‘u lavas. We present here a petrographic model for the petrogenesis of Ko‘olau-Makapu‘u basalts (Figure 38).

At time 1, the Ko‘olau-Makapu‘u component injects into the Loa-type cumulate mush at both the deep and shallow crustal magma reservoir(s) beneath the summit caldera, picking up high Fo olivine in the deep magma reservoir. The high-silica melt starts to react with the surrounding olivine-rich cumulate mush. However, not much time is allowed for reaction to occur before eruption. Thus, antecrystic high Fo olivine is retained, although resorbed and beginning to react. The material that erupts has not had time to dilute or assimilate wall rock material and reflects the peak Ko‘olau-Makapu‘u isotopic signature. This magma contains antecrystic, high-Fo olivine from the deep magma reservoir, high Mg# pyroxenes that crystallized at depth, and hotter, more primitive temperatures.

Over time, the high-silica Ko‘olau-Makapu‘u melt that did not erupt upon arrival continues to react with the Loa-type cumulate mush (time 2). In the shallow magma reservoir, low Fo olivine, clinopyroxene, and plagioclase that were present in the Loa-type cumulate mush resorb, and olivine and clinopyroxene form orthopyroxene reaction rims (Figure 38, T-2 inset). As olivine, clinopyroxene, and plagioclase react with the high-silica melt, orthopyroxene phenocrysts and glomerocrysts crystallize from the resulting mixture. As the Ko‘olau-Makapu‘u mixes and reacts with the Loa-type cumulate mush, the Ko‘olau-Makapu‘u isotopic signature dilutes, which drives isotopic compositions to relatively depleted compositions (decrease in $^{208}\text{Pb}/^{206}\text{Pb}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ and increase in $^{176}\text{Hf}/^{177}\text{Hf}$ and $^{143}\text{Nd}/^{144}\text{Nd}$). Assimilation of Loa-type wall rock also contributes to dilution of the Enriched Loa isotopic composition. At the same time, the mixture is fractionally crystallizing, which decreases pyroxene Mg# and temperatures.

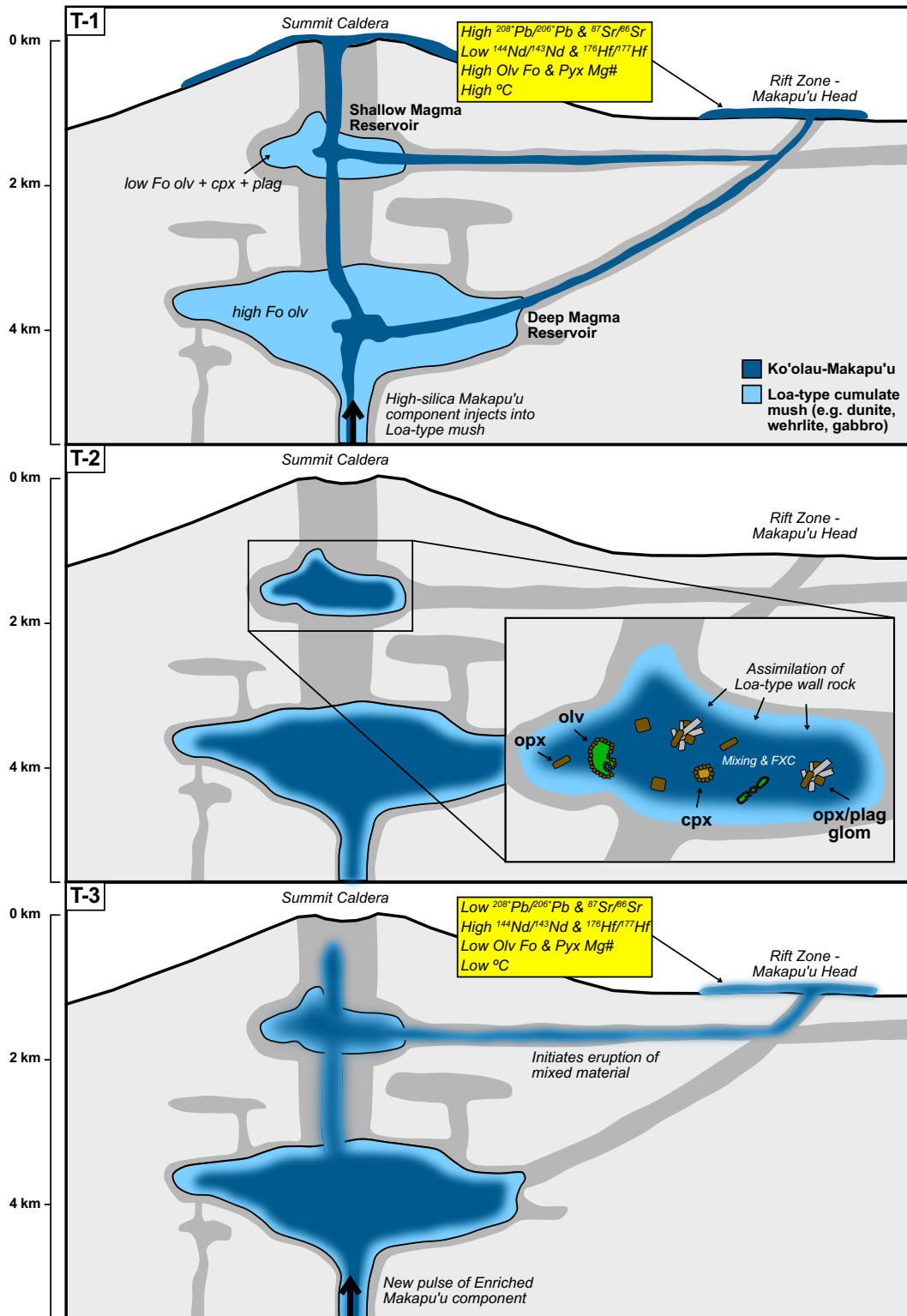


Figure 38: Petrologic model for petrogenesis of Ko'olau-Makapu'u basalts. T-1 indicates initial injection of Ko'olau-Makapu'u lavas into deep and shallow crustal reservoirs with pre-existing

cumulate mush of Loa-type compositions. T-2 indicates subsequent mixing and dilution and simultaneous fractional crystallization. T-3 indicates new pulse of Ko‘olau-Makapu‘u which triggers eruption of diluted lavas.

Eventually, the next recharge event of Ko‘olau-Makapu‘u compositions occurs (time 3), providing an eruption trigger for the isotopically diluted and evolved mixture of Ko‘olau-Makapu‘u and Loa-type composition to erupt. The initial eruption is the diluted and evolved melt, with relatively low olivine Fo, pyroxene Mg#, and temperatures and depleted Ko‘olau-Makapu‘u isotopic signature. Eventually, the Ko‘olau-Makapu‘u and Loa-type mixture will exsolve from the magma reservoir, and the peak expression of Ko‘olau-Makapu‘u will erupt.

The cyclic nature of Ko‘olau-Makapu‘u replenishment, mixing and dilution through time is reflected in the surface expression of cyclic mineral-scale chemistry and whole-rock isotopic compositions through stratigraphic order (Figure 5 and 37). One way to further test this petrologic model is through major and trace element modeling in Magma Chamber Simulator (Bohrson et al., 2020; Heinonen et al., 2020), a thermodynamic model for tracking the phase, thermal, and compositional evolution of an open-system magma chamber. Magma Chamber Simulator (MCS) will be used to test if melting of an eclogite or pyroxenite source into a typical Mauna Loa-like composition, with subsequent mixing and assimilation of Mauna Loa-like stoped blocks, will produce the whole-rock major and trace element compositions we see at Ko‘olau-Makapu‘u.

4.7 An Explanation for Lack of a Postshield Stage

Ko‘olau and Lāna‘i (two of the three Enriched Loa volcanoes) are the only volcanoes in the Hawaiian Islands that lack a postshield volcanic stage. Many of the current studies on Ko‘olau Volcano investigate the anomalous major and trace element compositions and enriched isotopic compositions compared to other Hawaiian volcanoes, in the context of source lithology

heterogeneity (e.g. Haskins and Garcia, 2004; Jackson et al., 2012; Williamson et al., 2025; Tanaka and Nakamura, 2002; Fekiacova et al., 2007, to name a few). This is the first study of Ko‘olau Volcano to investigate the petrologic response to magmas produced by a different mantle source and provide a potential explanation for the lack of a postshield stage at Enriched Loa volcanoes. This study has shown that the high-silica Ko‘olau-Makapu‘u melt strongly reacts with a Loa-type cumulate mush, rich in olivine, to form orthopyroxene. Since this reaction is unique to Ko‘olau-Makapu‘u, we investigate if this reaction could provide a potential explanation for the lack of a postshield stage.

The postshield volcanic stage typically involves magma reservoirs moving deeper in the crust, magma recharge declining, and eruptions becoming more infrequent and explosive than the shield stage (Clague and Sherrod, 2014). During the shield stage magma supply from the mantle is relatively sustained and may form reaction-armored pathways through the mantle that hasten the transit of magmas from the mantle to the surface. With the transition to the postshield stage, magma supply rates drop, fractionation proceeds beyond olivine control ($< 7 \text{ wt\% MgO}$) to consistently fractionate clinopyroxene and plagioclase, and the magma transit system becomes less centralized and more distributed. Trace elements La and Yb have been used to approximate relative degree of melting in Hawaiian lavas, because Yb is retained in garnet and remains stable through various degrees of melting, while La is highly incompatible, and will be present at higher concentrations with lower degrees of melting (Hofmann & Farnetani, 2013). Ko‘olau-Makapu‘u lavas have higher La/Yb than early main shield stage, Loa-type lavas at Ko‘olau, and thus, have lower degrees of melting (Figure 39).

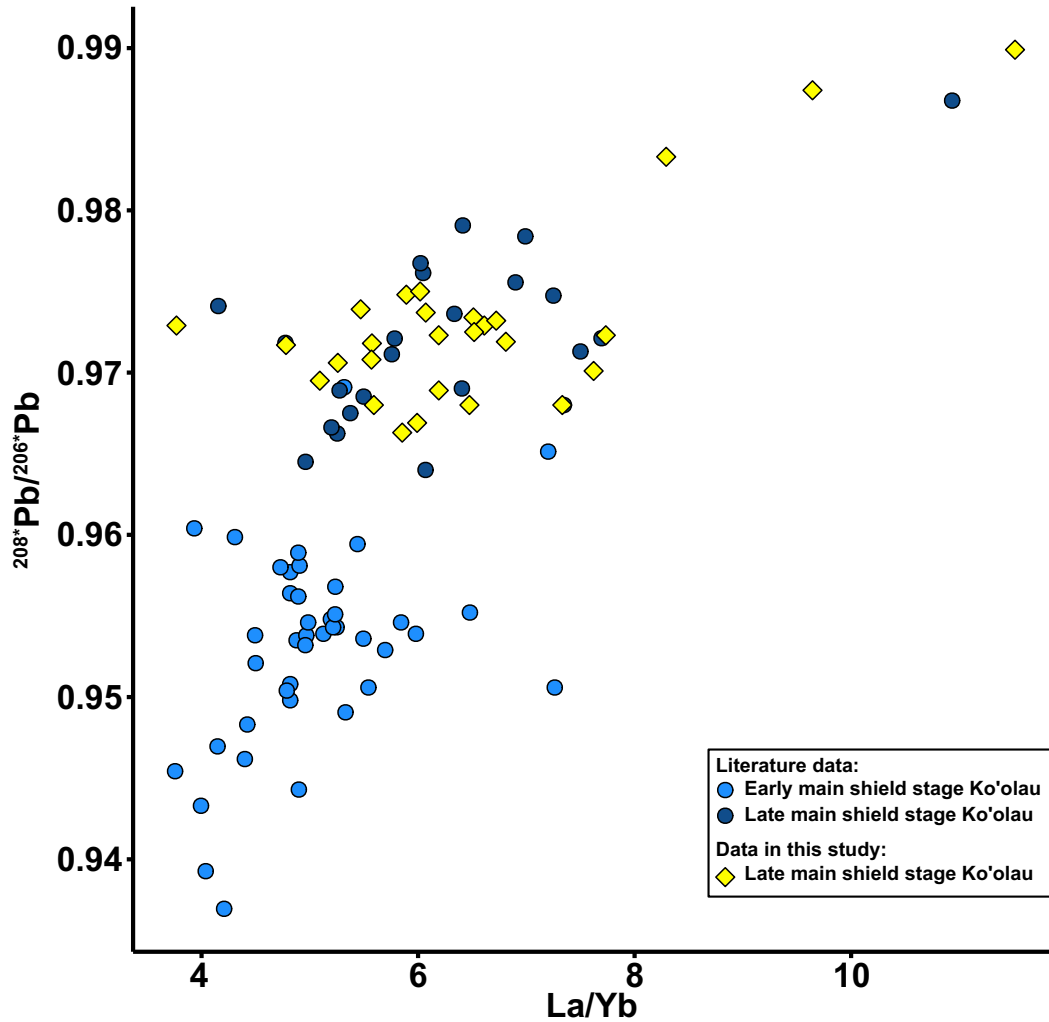


Figure 39: Radiogenic lead vs. La/Yb plot of early and late main shield stage Ko'olau basalts. High La/Yb of late shield stage indicates lower degrees of melting.

Lower degree melts that are high in silica would be expected to be generated at lower mantle potential temperatures than high degree melts from a peridotite because lithologic heterogeneity will produce melt at lower temperatures than a corresponding peridotite (Lambart et al., 2016). Therefore, the Ko'olau-Makapu'u parental melt may be slightly cooler than previous main-stage melts. At Ko'olau, this magmatic waning is accompanied by a change in mantle source that both decreases the temperature of recharge melts delivered to the magma system and is highly reactive with the pre-existing Loa-type cumulate mush. Without the

sustained replenishment of a high-MgO, equilibrium, Loa-type primitive magma to buffer the system at higher temperatures, the magma reservoir will inevitably crystallize faster, further compounded by the increased crystallization from mineral reactions, potentially preventing magmas from making it to the surface. This positive feedback loop may prematurely freeze the volcanic plumbing system before evolving into a postshield stage configuration. High SiO₂ reactive Ko‘olau-Makapu‘u melts will react similarly with an upper mantle harzburgite or peridotite as it would with a dunite or wherlite mush in the shallow Ko‘olau edifice. Therefore, the model of reactive magma freezing may be more systemic across the entire mantle melt column and magma transit pathways from the mantle into the edifice, drastically decreasing prematurely the magmatic flux delivered to the shallow plumbing system.

In addition to the lower degrees of melting and decrease in magma flux delivery, the reaction of high silica melt with the preexisting magma mush will have heat budget implications that may either keep the system molten longer or contribute to premature crystallization of the plumbing system. Thus, we calculate the enthalpy change for mineral-melt reactions that have occurred, as follows, using the experimentally derived enthalpy of formations for the different phases at 1200 K from Zen (1972):

$$\Delta H = \sum \Delta H_{f\ product}^o - \sum \Delta H_{f\ reactant}^o$$

The peritectic reaction of olivine and quartz to clinoenstatite is slightly exothermic when the enthalpies of formation of the different phases are calculated (-1.821 kJ/mol). However, the reactions are more complex than only the dissolution of olivine to form pyroxene. The lack of clinopyroxene macrocrysts suggests that any clinopyroxene in the system was also dissolved, for which, the consumption of clinopyroxene and quartz to form clinoenstatite is an endothermic

reaction (40.29 kJ/mol). With these two reactions occurring simultaneously, the overall formation of orthopyroxene is on net an endothermic reaction (39.469 kJ/mol). In other words, more heat is required to break the strong bonds of calcium in clinopyroxene than the latent heat of crystallization of orthopyroxene, resulting in a net cooling. Additionally, the dissolution of plagioclase would also result in net consumption of heat unless an equal volume of plagioclase re-crystallized after the magmatic heating event (Andrews, 2021).

This explanation for the lack of a postshield stage requires future work to fully developed. Models to quantify how much Ko‘olau-Makapu‘u melt would need to be injected into a Loa-type cumulate mush to react all available melt and never erupt could be calculated to test if this is a plausible or realistic explanation. This would require estimations on the magma reservoir size, which may be possible from geophysical datasets such as Bouger gravity anomaly size and spatial extent. Such work would also require additional constraints on storage depth and reservoir size, which are not currently available for Ko‘olau, but which do exist for other Hawaiian volcanos, such as Kīlauea (e.g. Weiser et al., 2020b) and Mauna Loa (e.g. Winslow et al., 2025). Finally, the exact volume and modal proportions of pre-existing mush zones and volume of recharge magmas are not known, and such parameters would be necessary to constrain the net heat effect of reactive mixing of Ko‘olau Makapu‘u silicious magmas with a preexisting Loa-type magma mush.

CHAPTER 5 – CONCLUSIONS

The lack of a postshield stage and distinct Pb-Sr-Nd-Hf (e.g. Williamson et al., 2025; Weis et al., 2020), major element, and trace element (e.g. Jackson et al., 2012) compositions of Ko‘olau-Makapu‘u basalts distinguish Ko‘olau Volcano from the rest of the Hawaiian chain. Previous whole-rock (Frey et al., 1994; Haskins and Garcia, 2004; Tanaka and Nakamura, 2002; Jackson et al., 2012) and isotopic (Fekiacova et al., 2007; Armstrong, 2022; Weis et al., 2020; Williamson et al., 2025) studies have suggested mixing between multiple magmas is required for the petrogenesis of Ko‘olau-Makapu‘u basalts, and melting of a pyroxenite or eclogite source can achieve the Ko‘olau-Makapu‘u geochemistry. This study shows that Ko‘olau Volcano’s mineral assemblage and shallow crustal reactions also contribute to Ko‘olau’s unique identity. This study provides, for the first time, a model for the petrogenesis of Ko‘olau-Makapu‘u basalts and a possible explanation for the lack of a postshield stage.

Ko‘olau-Makapu‘u basalts show strong disequilibrium textures and orthopyroxene reaction rims on olivine antecrysts, a texture that has never been documented in a Hawaiian volcano. This, along with complex mineral zoning and cyclic Ko‘olau-Makapu‘u isotopic signatures that temporally coincide with primitive pyroxene Mg#, olivine Fo, and temperature signatures suggest a high silica Ko‘olau-Makapu‘u melt was injected into the system at least three times to react with the olivine-rich, Loa-type cumulate mush. This study provides the first conceptual model for the shallow crustal reactions that contribute to the petrogenesis of Ko‘olau-Makapu‘u basalts, informed by mineral textures and chemistry. This aids in our general understanding of plumbing system dynamics at Hawaiian volcanoes and adds petrologic evidence for a plumbing system response to a heterogeneous mantle source material, greatly

contributing to the decades-long debate on the petrogenesis of Enriched Loa lavas. The olivine-high silica melt reaction in the shallow crustal magma reservoir(s) provides a possible explanation for the lack of a postshield stage, in which cooler, low-degree melts which participate in an endothermic reaction would effectively crystallize the magma in the volcanic edifice past the threshold to inhibit eruption. Future work to constrain the heat exchange of this reaction and calculations to quantify the amount of melt needed to react and cause the lack of a postshield stage are needed to constrain this theory. Furthermore, this petrologic model can be generally improved by magma storage depth constraints (e.g. melt inclusion barometry), isotopic mixing models, and a detailed comparison to other Enriched Loa volcanoes: Lānaʻi, which also lacks a postshield stage and Kahoʻolawe, which does not lack a postshield stage.

Koʻolau Volcano is undoubtedly unique on multiple chemical (Pb-Sr-Nd-Hf, major element, and trace element compositions) and physical (olivine-high silica melt reaction) scales. Although the cyclic magma rejuvenation and open-system processes recorded in Koʻolau-Makapuʻu basalts is non-unique for the dying of a Hawaiian shield volcano, the mantle heterogeneity recorded by Koʻolau Volcano's isotopic, major element, and trace element compositions initiates mineral-melt reactions in the shallow crustal magma reservoir(s) that have not been recorded in a Hawaiian volcano before, thus providing valuable insight into the influences of mantle source chemical heterogeneity on the petrogenesis of Hawaiian basalts.

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APPENDIX A – ELECTRON MICROPROBE ANALYTICAL CONDITIONS

EPMA spectrometers with crystal (TAP, LIF, PETJ, PETL, or LIFL) assignments and count-times (seconds) for each analyzed element on various analytical days for EPMA data collected at Colorado State University.

Analytical day	Phase analyzed	Spectrometers					Accelerating Voltage (kV)	Beam Current (nA)	Beam Size (μm)
		1 – TAP	2 - TAP	3 – LIF or PETJ	4 – PETL or LIFL	5 – PETL or LIFL			
Point data									
06/20/25 & 06/21/25	Olivine		Si (20) Mg (20) Al (40)	LIF Fe (30) Mn (50)	PETL Ca (50)	LIFL Ni (50)	20	20	0
08/12/25	Olivine	Si (20)	Mg (20) Al (60)	LIF Fe (20) Mn (60)	PETL Ca (60)	LIFL Ni (60)	15	50	1
08/15/25 & 08/16/25	Olivine	Si (20) Na (20)	Mg (20) Al (20)	LIF Fe (20) Mn (60)	PETL Ca (20) Ti (60)	LIFL Ni (60) Cr (20)	15	50	1
08/21/25	Olivine	Al (90) Si (10)	Al (90) Mg (10)	PETJ Mn (50) Ca (45)	PETL Ca (105)	LIFL Fe (45) Ni (55)	15	50	1
09/10/25 – 09/13/25	Pyroxene	Na (60) Al (60)	Mg (30) Si (30)	LIF Cr (60) Fe (30)	LIFL Mn (60) Ni (60)	PETL Ca (30) Ti (60)	15	20	1
09/16/25	Olivine	Al (60)	Mg (30) Si (30)	LIF Fe (30)	LIFL Mn (40) Ni (40)	PETL Ca (40)	15	20	1
10/22/25 – 10/25/25	Olivine & Pyroxene	Al (60) Na (60)	Mg (30) Si (30)	LIF Cr (60) Fe (30)	LIFL Mn (60) Ni (60)	PETL Ca (30) Ti (60)	15	20	1

<i>Analytical day</i>	<i>Phase analyzed</i>	<i>Spectrometers</i>					<i>Accelerating Voltage (kV)</i>	<i>Beam Current (nA)</i>	<i>Beam Size (μm)</i>
		<i>1 – TAP</i>	<i>2 - TAP</i>	<i>3 – LIF or PETJ</i>	<i>4 – PETL or LIFL</i>	<i>5 – PETL or LIFL</i>			
01/26/26	Olivine & Pyroxene	Al (40) Si (30)	Mg (30) Na (40)	LIF Mn (40) Fe (30)	LIFL Ni (40) Cr (40)	PETL Ca (30) Ti (40)	15	20	2
01/26/26	Plagioclase	Al (20) Si (20)	Mg (30) Na (20)	LIF Mn (20) Fe (20)	LIFL Ti (40)	PETL Ca (20) K (30)	15	12	0-2
04/23/26	Pyroxene	Si (30) Mg (30)	Al (30) Na (30)	LIF Fe (40) Mn (40)	LIFL Ni (40) Cr (40)	PETL Ti (40) Ca (40)	15	20	2
<i>OSAT Point Data</i>									
10/23/25	Spinel	Mg (20)	Si (30) Al (20)	LIF Fe (20) Cr (20)	LIFL Mn (30) Ni (30)	PETL Ti (30)	15	20	1
10/23/25	Olivine – Stage 1	Mg (20)	Si (20)	LIF Fe (20)	LIFL Mn (30) Ni (30)	PETL Ca (30)	15	40	5
10/23/25	Olivine – Stage 2	Al (60)	Al (60)	LIF Cr (60)	LIFL Cr (60)	PETL P (60)	15	150	5
<i>Pyroxene Maps</i>									
Stage 1	Pyroxene	Si (30)	Na (40)	LIF Fe (30)	LIFL Cr (40)	PETL Ti (40)	15	20	0
Stage 2	Pyroxene	Al (40)	Mg (30)	LIF Mn (40)	LIFL Ni (40)	PETL Ca (30)	15	20	0