

**COMPLEX GARNET ZONING FROM LAWSONITE ECLOGITE FROM
SOUTH OF THE MOTAGUA SUTURE ZONE, GUATEMALA**

A Dissertation Presented to
the Faculty of the Department of Earth & Atmospheric Sciences
University of Houston

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

By
Deborah Raeann Bradley

May 2019

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Abstract

Serpentinite mélange of the Guatemalan suture zone hosts the exhumed remains of one of the coldest subduction zones in the world. The mélange contains several different metamorphic rocks, including lawsonite eclogite. Well-preserved lawsonite eclogite is particularly rare, and is preserved only in high-pressure, low-temperature metamorphism wherein exhumation is rapid. Though lawsonite eclogite is well-preserved, the full extent of the P-T-t path this HP-LT rock experienced is contentious, with two competing proposed P-T paths: one with a prograde path with garnet growth from 300 to 480 °C at 1.1-2.6 GPa, and another with a prograde path from 470 to 520 °C at 2-2.5 GPa. Combining major, trace, and rare earth element (REE) garnet concentrations with crystal size distribution analysis, X-ray element maps, REE modeling, and Sm-Nd age data, constraints are placed on the prograde P-T-t path of these HP-LT metabasites. My data reveal a complex zoning in major, trace, and rare earth elements. Core to rim concentration profiles define normal prograde zoning, but deviated from this zoning towards the rim, with restricted regions of complex zoning in garnet compatible elements (e.g., Mn and HREEs), with a decrease of these elements at the rim. This complex zoning is related to changes in bulk composition, fluid availability, and garnet growth rate, which indicates that garnet experienced different stages of growth over a protracted period, perhaps as long as 33 Ma. The overall variability of chemical zoning between eclogite samples in the mélange, it is also apparent that different P-T histories may be recorded in different eclogite blocks.

Table of Contents

1. Introduction	1
1.1. References	4
2. Analysis of major and trace elemental zoning for garnet in lawsonite eclogite from the southern Guatemalan suture zone: evidence for multi-stage garnet growth.	6
2.1. Introduction	6
2.2. Geological Setting and Sample Selection	8
2.3. Methods	9
2.4. Petrography	11
2.5. Results	14
2.5.1. Major Element Zoning	14
2.5.2. Crystal Size Distribution	18
2.5.3. Trace Element Zoning	19
2.6. Discussion	21
2.6.1. Element Zoning	21
2.6.2. Crystal Size Distribution	29
2.6.3. Evidence for multi-stage growth	29
2.7. Implications	33
2.8. References	35
3. Complex Garnet Zoning May Reflect A Simple Subduction History	44
3.1. Introduction	44
3.2. Geological Setting	47
3.3. Methods	48
3.4. Results	50
3.5. Discussion	54
3.6. References	59

4. Variability of major and trace element zoning for garnet in different lawsonite eclogite samples from the Guatemalan suture zone suggests unique P-T history between eclogite samples.	65
4.1. Introduction	65
4.2. Geological Setting	68
4.3. Methods	70
4.3.1. Major Element Concentration	70
4.3.2. Trace and REE Concentration	71
4.3.3. X-ray Element Maps	71
4.3.4. Sample Preparation for Sm-Nd Isotopic Analysis	72
4.3.5. Leaching Sm-Nd Isotopic Analysis	72
4.3.6. Digestion and Analysis	73
4.4. Petrography	74
4.4.1. MVE12-66-1	74
4.4.2. MVE12-66-4	76
4.4.3. MVE12-66-5	77
4.4.4. MVE12-66-7	79
4.4.5. MVE12-67-1	81
4.4.6. MVE12-68-3	83
4.5. Results	84
4.5.1. Major Element	84
4.5.2. Trace Element Zoning	96
4.5.3. Age Data	108
4.6. Discussion	109
4.6.1. Major Element Zoning Variance	109
4.6.2. Trace Element Zoning Variance	112
4.6.3. A Complex History	113
4.6.4. Providing Constraints on Timing of Peak P-T	116
4.7. Further Avenues of Research	119

4.8. Concluding Remarks	120
4.9. References	122
Appendix A	135

List of Figures

1.1	Geological map of the Motagua suture zone area	2
2.1	Combined petrological data for Type-I Lawsonite Eclogite	12
2.2	Garnet end member zoning profiles for MVE12-66-1.4, MVE12-66-4-003.6, and MVE12-66-4-002.1	14
2.3	X-ray element map of wt% MnO for MVE12-66-1.5 and Lu zoning	17
2.4	Crystal size distribution for MVE12-66-1	18
2.5	REE zoning for MVE12-66-1.4, MVE12-66-1.5, and MVE12-66-4-002.1	20
2.6	Calculated P-T path from Tsujimori et al. 2006b	23
2.7	Sr zoning in MVE12-66-1	29
2.8	REE composition of lawsonite in MVE12-66-4	31
2.9	Mineral paragenesis for Type-I lawsonite eclogite	33
3.1	Map of the Motagua Suture Zone	45
3.2	X-ray element map for MnO for garnet sample MVE12-66-1.5	50
3.3	Calculated chemical zoning profiles for Lu	51
3.4	Comparison of P-T paths for complexly zoned garnet	56
4.1	Geological map of the Motagua suture zone area	68
4.2	Thin section images of MVE12-66-1	74
4.3	Thin section images of MVE12-66-4	76
4.4	Thin section images of MVE12-66-5	77
4.5	Thin section images of MVE12-66-7	79
4.6	Thin section images of MVE12-67-1	81
4.7	Thin section images of MVE12-68-3	83
4.8	Garnet end member profile of MVE12-66-1.6	85
4.9	Garnet end member profile of MVE12-66-4-003.3	86
4.10	Garnet end member profile of MVE12-66-4-003.7	87
4.11	Garnet end member profile of MVE12-66-4-003.9	88
4.12	Garnet end member profile of MVE12-66-7.1	89

4.13	Garnet end member profile of MVE12-66-7.3	90
4.14	Garnet end member profile of MVE12-66-7.4	91
4.15	Garnet end member profile of MVE12-66-7.5	92
4.16	X-ray element maps for MVE12-66-1.5 and MVE12-66-7.5	94
4.17	Trace element profiles for MVE12-66-1	98
4.18	REE profiles for MVE12-66-7	101
4.19	Trace element profiles for MVE12-66-7.5	104
4.20	REE diagram for lawsonite in MVE12-66-7	106
4.21	Age data for MVE12-66-1	109
4.22	Multi-cyclic subduction P-T paths	114
4.23	P-T paths for south Motagua eclogites	115
4.24	Model for subduction and exhumation of lawsonite eclogite	118

List of Tables

2.1	Trace element data for lawsonite in MVE12-66-4	25
2.2	REE data for lawsonite in MVE12-66-4	26
2.3	REE data for garnet in MVE12-66-1 and MVE12-66-4	27
2.4	Trace element data for two garnet zones in MVE12-66-1	32
4.1	Trace element concentration for MVE12-66-1.4	96
4.2	Trace element concentration for MVE12-66-1.5	96
4.3	Rare Earth Element concentration for garnet in MVE12-66-7.3	99
4.4	Rare Earth Element concentration for garnet in MVE12-66-7.5	100
4.5	Trace element concentration for garnet in MVE12-66-7.5	103
4.6	Trace element data for lawsonite for MVE12-66-7	105
4.7	Trace element compositions for phengite in MVE12-66-7	107
4.8	Sm and Nd element and isotope data for MVE12-66-1	108
A.1	Major Element Zoning for MVE12-66-1.4	135
A.2	Major Element Zoning for MVE12-66-1.5	137
A.3	Major Element Zoning for MVE12-66-1.6	139
A.4	Major Element Zoning for MVE12-66-4-002.1	141
A.5	Major Element Zoning for MVE12-66-4-003.3	143
A.6	Major Element Zoning for MVE12-66-4-003.6	145
A.7	Major Element Zoning for MVE12-66-4-003.7	147
A.8	Major Element Zoning for MVE12-66-4-003.9	149
A.9	Major Element Zoning for MVE12-66-7.1	151
A.10	Major Element Zoning for MVE12-66-7.3	153
A.11	Major Element Zoning for MVE12-66-7.4	155
A.12	Major Element Zoning for MVE12-66-7.5	157

Chapter 1: INTRODUCTION

Developing a full understanding of the development of a subduction zone can be a complex task. Depending on the P-T conditions the subducting material experiences, it can be difficult to build a full picture of the prograde and retrograde path of much of the highest-grade metamorphic assemblages, as it is difficult to exhume these rocks from the coldest subduction zones (Hernández-Urbe and Palin, 2019). Therefore, in places where these assemblages are not only exhumed, but also well preserved without either overprinting or retrograde processes, it is imperative to approach these samples using a wide range of analytical techniques in order to understand their history. In the case of lawsonite eclogite from the south Motagua suture zone (Figure 1.1), garnet serves as the key refractory mineral that preserves a wealth of data that can be used to determine processes going on during the prograde portion of the P-T path for subduction zones. My study revolved around several eclogite samples all collected within tens of meters from each other. Presumably, they all underwent a similar subduction history. Any observed differences or similarities are used to understand this relict subduction zone.

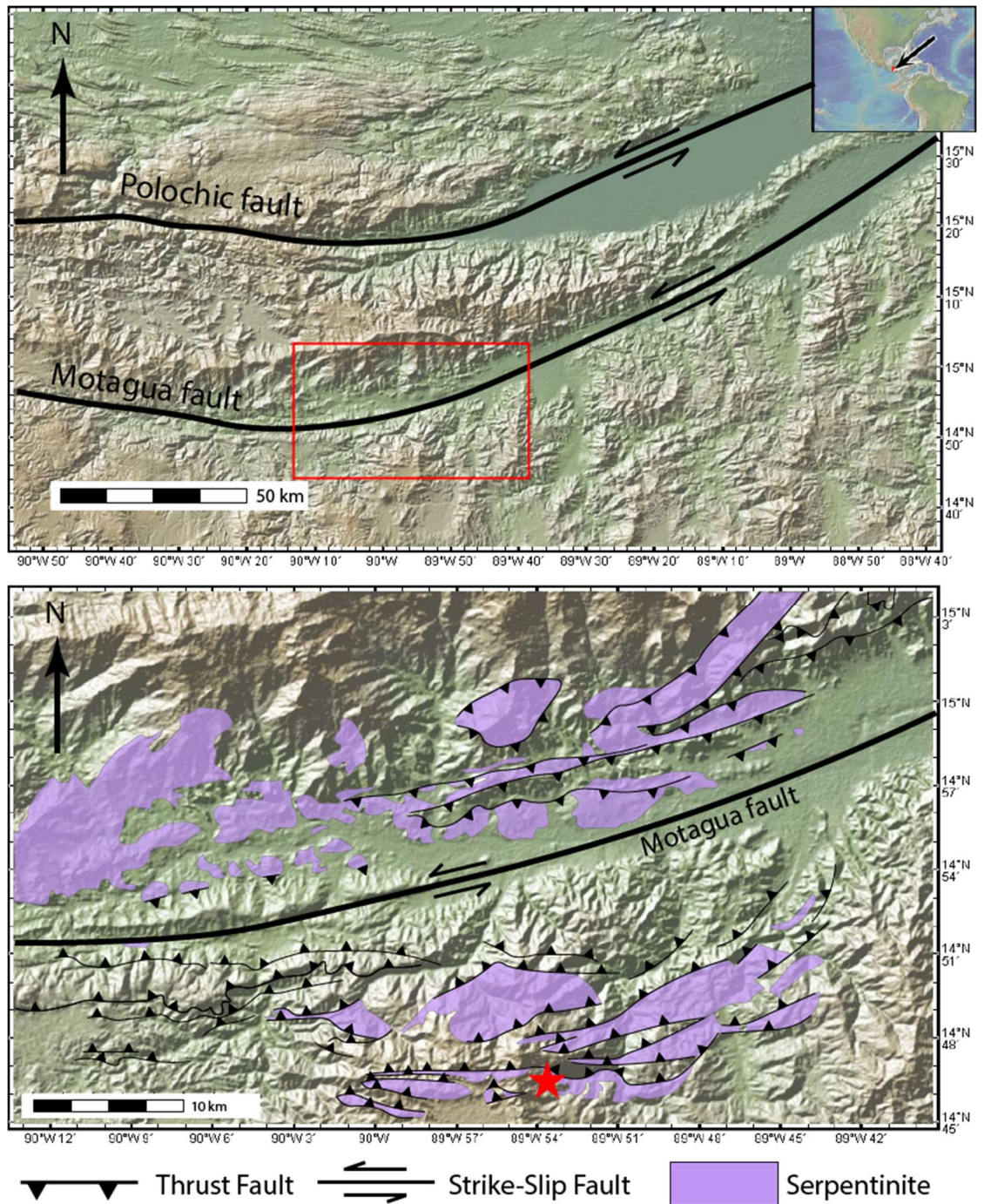


Figure 1.1: The Motagua fault is a left-lateral strike-slip fault located in central Guatemala. Red star indicates location of my samples. This map was modified from an original, unpublished map by Sisson (personal communication, 2014).

In Chapter 2, major, trace, and rare earth element (REE) concentration zoning of garnet and petrographic analysis of eclogite samples MVE12-66-1 and MVE12-66-4 are combined with crystal size distribution analysis of MVE12-66-1 in order to determine the cause for complex chemical zoning in garnet. These two eclogite samples were examined together due to the similarity between the chemical zoning of garnet in both eclogite samples, suggesting that both eclogite samples experienced the same prograde history with regards to processes governing garnet growth and variations in pressure and temperature.

In Chapter 3, rare earth element zoning modeling was conducted using Lu for two different temperature histories calculated for southern Motagua eclogites: One being 300-480 °C (Tsujimori et al., 2006), and the other being 470-520 °C (Endo et al., 2012). The purpose of modeling Lu is that, by using an element highly compatible in garnet, I can determine the effects of different growth mechanisms of garnet as well as temperature on the chemical zoning recorded by garnet growth. Furthermore, with two competing P-T histories, these growth models can help decide which pressure-temperature path better fits the calculated concentration zoning and thus reproduce the observed chemical zoning of that element in garnet. The concentration zoning of Lu in MVE12-66-1.4 was used due to the preservation of both core concentration and the increase of HREEs at the rim of garnet.

In Chapter 4, major, trace, and REE concentration zoning of garnet is combined with petrographic analysis of MVE12-66-1, MVE12-66-4, and MVE12-66-7 to explain the variability in chemical zoning preserved in these eclogite samples. Though MVE12-

66-1 and MVE12-66-4 are quite similar, MVE12-66-7 is different in both chemical zoning of garnet and texturally. These variations suggest that the subduction zone itself has some variability in processes at work during prograde metamorphism. This variability is recorded by the differences in both chemical zoning and the inclusions found in garnet. Sm-Nd age of garnet for MVE12-66-1 is also determined, with the garnet portion analyzed being biased to the rim portion.

Combining all of these analyses, it can thus be determined how this lawsonite eclogite developed during prograde metamorphism. Furthermore, analyzing more than one eclogite sample, particularly significantly different eclogite samples, produces a more complete picture of the subduction zone and highlights the complexity of subduction zones. Overall, it can be determined that garnet in lawsonite eclogite can have complex zoning with a simple subduction and exhumation history. This complex zoning can be explained in changes in bulk composition and nutrient availability, which both can have a significant affect on the composition preserved by garnet.

1.1: References

Endo, S., Wallis, S.R., Tsuboi, M., Torres de León, R., and Solari, L.A. (2012) Metamorphic evolution of lawsonite eclogites from the southern Motagua fault zone, Guatemala: Insights from phase equilibria and Raman spectroscopy. *Journal of Metamorphic Petrology*, 30, 143-164.

Hernández-Uribe, D., and Palin, R.M. (2019) A revised petrological model for subducted oceanic crust: Insights from phase equilibrium modeling. *Journal of Metamorphic Petrology*. Advance online publication. doi: 10.1111/jmg.12483.

Tsujimori, T., Sisson, V.B., Liou, J.G., Harlow, G.E., and Sorensen, S.S. (2006) Petrologic characterization of Guatemalan lawsonite eclogite: Eclogitization of subducted oceanic crust in a cold subduction zone. *Geological Society of America Special Papers*, 403, 147-168.

Chapter 2: ANALYSIS OF MAJOR AND TRACE ELEMENTAL ZONING FOR GARNET IN LAWSONITE ECLOGITE FROM THE SOUTHERN GUATEMALAN SUTURE ZONE: EVIDENCE FOR MULTI-STAGE GARNET GROWTH

Submitted for publication in American Mineralogist, March 2019

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2.1: INTRODUCTION

The serpentinite mélange in the southern Guatemalan suture zone is one of approximately twenty known locations in the world where lawsonite eclogite may be found (Tsuji-mori et al., 2006a). The presence of this rare metamorphic rock gives clear indication of high pressure, low temperature metamorphic conditions. Indeed, current P-T path calculations for these HP-LT rocks indicate a peak temperature of ~470 °C and a peak pressure of 2.6 GPa, with a calculated geothermal gradient of ~5 °C/km (Tsuji-mori et al., 2006b). Lawsonite eclogite from the southern Guatemalan suture zone provides a rare opportunity to study the geochemical and petrological evolution of metamorphic rocks in one of the coldest subduction zones on Earth (Harlow et al., 2004; Tsuji-mori et al., 2006a; Tsuji-mori et al., 2006b; Harlow et al., 2011).

The processes governing garnet growth and chemical composition in this low temperature, high-pressure metabasite are still not fully understood. The composition of garnet is sensitive to changes in pressure and temperature. For instance, Blanco-Quintero et al. (2011) calculated two prograde and retrograde paths from zoned garnet, which showed a complex, oscillatory, zoning for major elements in garnet. The relatively slow diffusion of major and trace element cations through garnet in high-P/low-T units (Caddick et al., 2010) preserves the chemical zoning patterns that form in response to changes in pressure, temperature, and matrix composition over what can amount to several million years (e.g., Lapen et al., 2003; Konrad-Schmolke et al., 2005; Skora et al., 2006; Skora et al., 2015; Kohn, 2009; Brueckner et al., 2009; Zhou et al., 2011). Therefore, garnet is particularly useful for understanding physical history and geochemical changes and makes it one of the most valuable minerals used to construct the pressure-temperature history of metamorphic rocks (e.g., Spear and Selverstone, 1983; Spear et al., 1984; Reinecke, 1998; Konrad-Schmolke et al., 2007).

Though garnet can serve as an excellent record of metamorphic events (Mezger et al., 1992; Herwartz et al., 2011; Dragovic et al., 2012), it is this same sensitivity to changes in temperature, pressure, and composition that make garnet a particularly difficult mineral to study with regards to the timing and rate of crystal growth (Konrad-Schmolke et al., 2007; Caddick et al., 2010; Blanco-Quintero et al., 2011). However, if the mechanisms governing growth of garnet in a particular sample can be defined, then the zoning patterns resulting from these mechanisms can be used to further refine P-T-t paths for a given sample (Lasaga and Jiang, 1995; Skora et al., 2006; Skora et al., 2015).

In this paper, I investigate what mechanisms are at work in creating the complex chemical zoning in garnet using both major and trace element zoning as well as crystal size distribution of the garnet samples in question (e.g., Skora et al., 2006).

2.2: GEOLOGICAL SETTING AND SAMPLE SELECTION

The Motagua fault is one of three E-W trending strike-slip faults in the Guatemalan suture zone cutting across central Guatemala that serves as the boundary between the Maya block of the North American plate to the north and the Chortís block of the Caribbean plate to the south. This suture zone is bound to the north and the south by two belts of serpentinite *mélange* that contain blocks of high-pressure, low-temperature rocks (Harlow et al., 2004). Sm-Nd dating of eclogite from both sides of the fault show that the timing of formation for these metamorphic rocks occurred between 140 and 120 Ma, suggesting the possibility that the serpentinite *mélanges* on both sides of the fault originated from the same tectonic event (Brueckner et al., 2009). Though these *mélange* belts appear to be similar, perhaps even genetically related, recent research indicates that these two regions experienced their own distinct metamorphic histories (Harlow et al., 2004; Brueckner et al., 2009; Ratschbacher et al., 2009; Martens et al., 2012). In particular, $^{40}\text{Ar}/^{39}\text{Ar}$ phengite ages for jadeitite and eclogite of 77-65 Ma and U-Pb zircon ages of 95 Ma (Flores et al., 2017) north of the fault and 125-113 Ma south of the fault, indicating a more complex metamorphic history on the north side. South of the fault, the lawsonite eclogites hosted in serpentinite *mélange* are thought to have experienced only the one major tectonic event (Harlow et al., 2004). Geochemical analyses and garnet grain size distribution of lawsonite eclogite samples from the south

side of the fault indicate that this model of simple prograde and retrograde history may be more complex than initially hypothesized.

Samples selected for this study are lawsonite eclogite samples MVE12-66-1 and MVE12-66-4. These samples were collected as float in a creek bed near the Carrizal Grande area within meters of each other. Since these samples were not collected in-situ, it is unlikely that they originate from the same eclogitic block.

2.3: METHODS

Electron probe microanalyses (EPMA) of garnet samples were conducted using the Cameca SX50 electron microprobe at the University of Houston. Quantitative analyses for major element concentration profiles were conducted with 15 kV accelerating voltage at 20 nA beam current, with a 10 μm spot size. Standard calibration was conducted using the University of Houston garnet standard. Profiles were created by spot analysis every 15 μm , skipping over detectable mineral inclusions and fractures. Conversion of weight % oxide into mole fraction was completed using MINERAL (De Angelis and Neill, 2012).

In situ trace element analyses were performed using a PhotonMachines Analyte.193 laser ablation instrument coupled to a Varian 810-MS quadrupole ICP-MS at the University of Houston. Prior to analysis, major element composition was measured by EPMA at the University of Houston. Trace element and REE analysis includes: ^7Li , ^{11}B , ^{25}Mg , ^{29}Si , ^{29}Sc , ^{51}V , ^{52}Cr , ^{55}Mn , ^{59}Co , ^{88}Sr , ^{89}Y , ^{91}Zr , ^{93}Nb , ^{95}Mo , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{149}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{173}Yb , ^{175}Lu ,

and ^{178}Hf . Garnet was analyzed with a spot size of 50 μm and lawsonite with a spot size of 15 μm . Each analysis was preceded by a gas blank of ~ 18 s. Samples were then ablated for ~ 25 s with a laser power of 3 mJ at a 4 ns pulse with a repetition rate of 10 Hz for garnet and 12 Hz for lawsonite. All trace element data was corrected for laser and ICP-MS element fractionation with internal elements Mg for garnet and Si for lawsonite calibrated by EPMA and USGS external standard BHVO-2G glass using the commercial data reduction software Glitter.

CT data was collected at the University of Texas Computed Tomography (UTCT) lab. Two CT scans were completed on their North Star Imaging scanner. Scans were collected with a Feinfocus source under high power at 210 kV, 0.26 mA, with an aluminum filter. A Perkin Elmer detector was used with a 0.5 pF gain, at 2 fps, no binning, no flip, with a source to object distance of 83.801 mm, and a source to detector distance of 1015 mm. This data was gathered over a continuous CT scan with no frames averaged, 0 skip frames, 7200 projections, 7 gain calibrations, a 5 mm calibration phantom, with a data range of -10, 270, and a beam-hardening correction of 0.175. Voxel size was 0.026 mm, requiring 2021 slices.

Grain size distribution analysis using CT scan data was conducted using Blob 3D (Ketcham, 2005). Voxel size of 0.026 mm was used to determine slice spacing. Grain size distribution for MVE12-66-1 was determined using measurements of 141 garnet grains.

X-ray elemental maps were collected using a Cameca SX100 electron microprobe at the American Museum of Natural History. Elemental analysis includes maps for Si, Ti,

Al, Mg, Mn, Ca, Fe, K, Na, and Ba. Analysis conditions include a beam current of 80 nA, an accelerating voltage of 15 Kv, a dwell time of 85 ms, a beam diameter of 1 μm , with a step size of 3 μm . Chemical data were used to create quantitative x-ray element and mineral maps with XMapTools version 2.5.2 (Lanari et al., 2014; Lanari et al., 2018).

2.4: PETROGRAPHY

Detailed petrography of lawsonite eclogite from the southern Guatemalan suture zone has been described by Tsujimori et al. (2006b). Their research divided the lawsonite eclogite in this region into three categories: Jadeite-bearing lawsonite eclogites, Type I lawsonite eclogites, and Type II lawsonite eclogites. Jadeite-bearing lawsonite eclogites are further divided into two categories: coarse and fine-grained rocks. Coarse-grained jadeite-bearing lawsonite eclogite is characterized by the presence of two generations of jadeitic pyroxene coexisting with garnet, rutile, phengite, chlorite, ferroglaucofane, lawsonite, titanite, ilmenite, and quartz. This type of lawsonite eclogite has garnet with an S_1 fabric preserved as inclusions in garnet, and an S_2 foliation present in the matrix. Fine-grained jadeite-bearing lawsonite eclogite contains smaller garnet grains, with omphacite, lawsonite, jadeite, phengite, quartz, and rutile. Unlike the coarse-grained variety, the inclusion trail defining S_1 is not preserved, with only S_2 foliation being preserved in the matrix. Type I lawsonite eclogites are described as containing omphacite, garnet, lawsonite, chlorite, titanite, phengite, and quartz. The matrix has weakly preserved S_2 and S_3 schistosity, with garnet grains lacking any preserved fabrics. Garnet grains in this type of eclogite have been described as having inclusion-rich cores, with relatively inclusion-free rims. Type II lawsonite eclogites contain an abundance of glaucophane in

the matrix along with omphacite, garnet, lawsonite, titanite, phengite, chlorite, and quartz. A penetrative S_3 foliation is preserved by prismatic omphacite with glaucophane and lawsonite. Garnet in this eclogite type also have inclusion-rich cores and inclusion-free rims with the internal fabric preserved in garnet being discontinuous with S_3 preserved by the matrix.

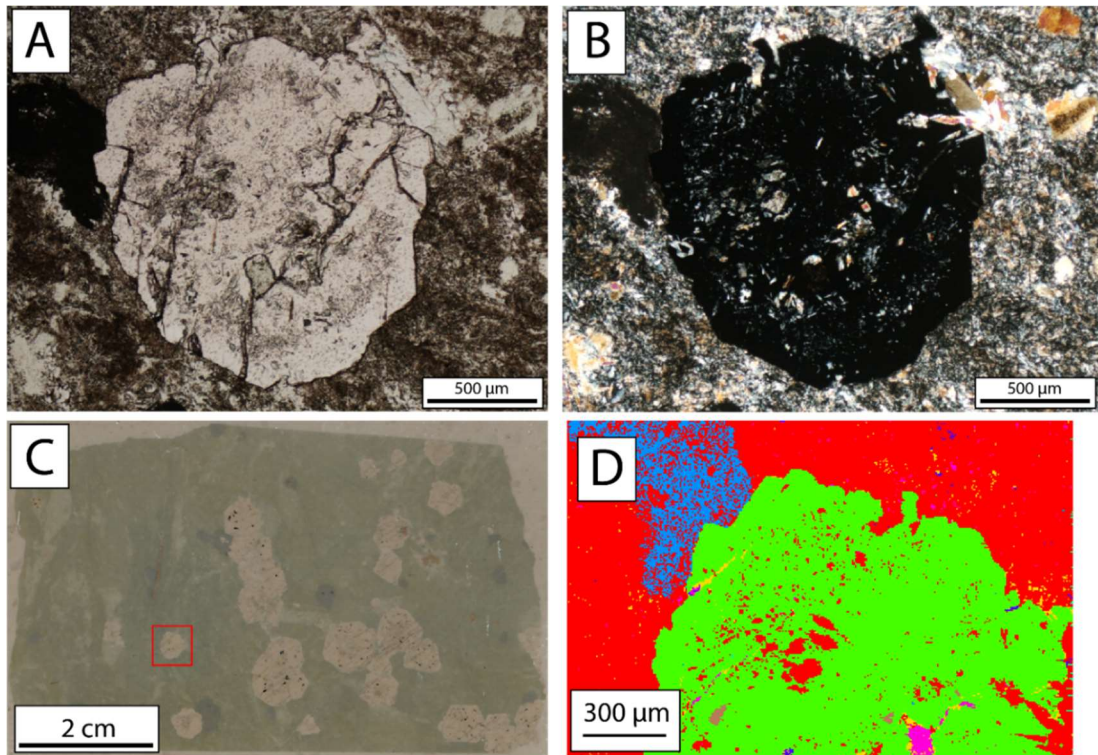


Figure 2.1: Combined petrological data for Type-I Lawsonite Eclogite (Tsujimori et al., 2006b) MVE12-66-1. A, B) Plane-polarized and cross-polarized light images of MVE12-66-1.5, with inclusions of lawsonite, omphacite, chlorite, and albite. C) Thin section scan of MVE12-66-1, showing layers of garnet, with a red box indicating the garnet analyzed: MVE12-66-1.5. D) Mineral identification done in XMapTools, showing a wide assortment of mineral inclusions in garnet. Pink = albite, purple = phengite, blue = titanite, brown = lawsonite, green = garnet, yellow = chlorite, and red = omphacite. Not all mineral inclusions described in the petrography are visible in this mineral map.

In this study, the two eclogite samples, MVE12-66-1 and MVE12-66-4, contain 2-5 mm in diameter garnet porphyroblasts that, on average, are smaller than those

described in Tsujimori et al., 2006b. They are typically idioblastic with few subidioblastic grains occurring near larger porphyroblasts or aggregates of somewhat smaller garnet crystals. Garnet is hosted in a weakly foliated matrix composed dominantly of omphacite with lawsonite and lesser chlorite, rutile, titanite, and phengite (Figure 2.1). All garnet samples examined here have inclusion-rich cores with inclusion assemblages that include ilmenite, omphacite, chlorite, lawsonite, phengite, rutile, and minor albite. The garnet rims are characterized by an inclusion-poor zone (Figure 2.1). Chlorite occurs predominantly as inclusions at the core of garnet, but also serves as fracture fill along with phengite. Lawsonite, too, is well preserved as idioblastic inclusions in the cores of garnet, and as xenoblastic grains in the matrix and in veins, but they are not present as inclusions at the rim of garnet. Ilmenite inclusions are found throughout garnet, except at the rim. Titanite occurs as well-preserved idioblastic overgrowths around rutile crystals in MVE12-66-1, and as poikilitic, xenoblastic porphyroblasts in both samples. Sample MVE12-66-1 contains lawsonite veins that also contain quartz and some xenoblastic garnet. MVE12-66-4 contains minor amounts of lens-shaped quartz grains that are randomly oriented. Based on the petrography, the eclogite samples studied here are most closely related to Type-I lawsonite eclogites as described by Tsujimori et al. (2006b).

2.5: RESULTS

2.5.1: Major Element Zoning

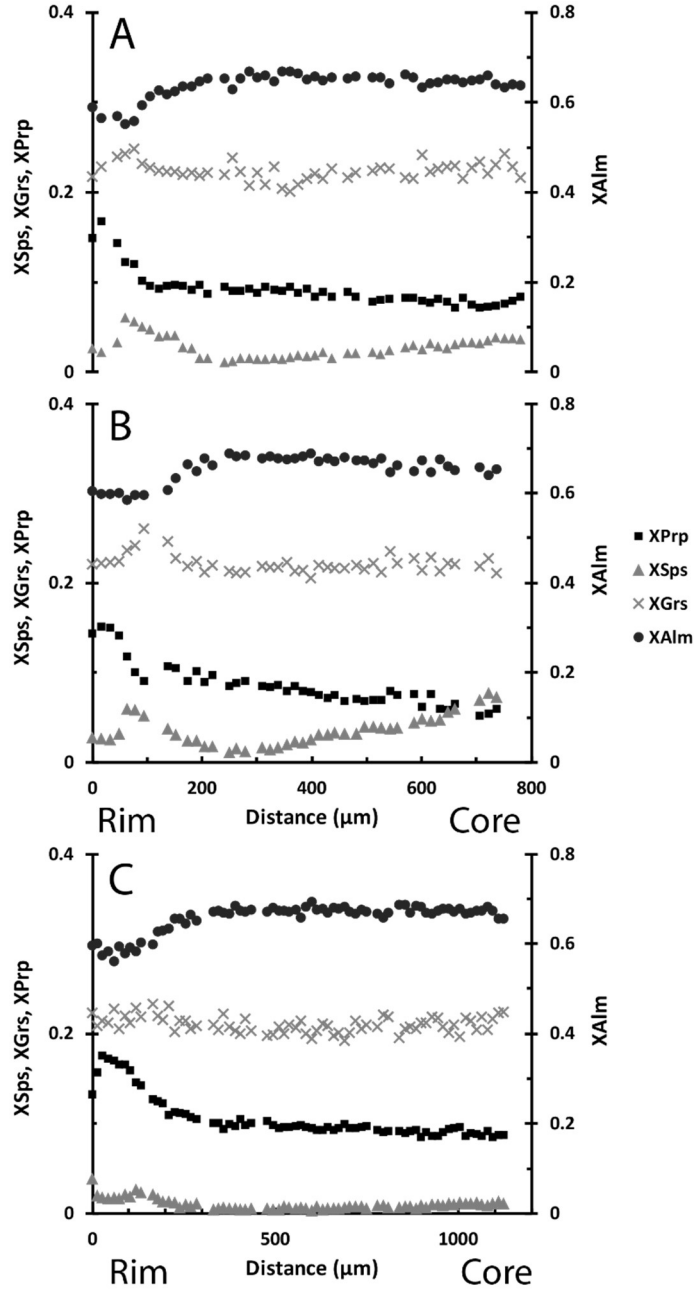


Figure 2.2: Garnet end member zoning profiles for three garnet grains, including: A) MVE12-66-1.4 (sample A), B) MVE12-66-4-003.6 (sample B), and C) MVE12-66-4-002.1 (sample C).

Major element compositional profiles for garnet from both eclogite samples are similar (Figure 2.2). Garnet samples are almandine-rich with a major component of grossular and both pyrope and spessartine as lesser components. Both garnet samples A (Figure 2.2 A) and B (Figure 2.2 B) contain small, localized increase and decrease in their grossular contents at approximately 100 μm from the rim of the grain.

Almandine compositions are also very similar, with A (Figure 2.2 A) and C (Figure 2.2 C) containing similar X_{Alm} of approximately 0.65. Garnet sample B (Figure 2.2 B) has a slightly lower X_{Alm} at its core, at approximately 0.63. These concentrations remain nearly homogeneous across much of the garnet grain. However, there is a significant decrease of X_{Alm} when approaching the rim beginning at approximately 300 μm from the rim in sample C (Figure 2.2 C), and beginning at approximately 200 μm from the rim in both sample A (Figure 2.2 A) and sample B (Figure 2.2 B). Relative to the garnet size, the change in X_{Alm} is about the same normalized distance from the core. The major difference in this zoning between each garnet sample is the distinct and abrupt decrease of X_{Alm} by 0.08 shown by sample B (Figure 2.2 B) when compared to the more gentle decrease shown by the other two samples.

The zoning profiles with respect to pyrope content are almost identical in all the analyzed garnet. Sample A and sample C are almost identical in pyrope content with approximately 0.08 X_{Prp} in the core of the garnet grains and ~ 0.14 X_{Prp} at the rim. Sample B has a lower X_{Prp} in its core relative to the other two garnet samples, with 0.06 X_{Prp} . However, this sample reaches X_{Prp} in line with those measured for the other two garnet grains at the rim. Most notable about this compositional profile is the small zone

of increase and decrease in pyrope within 100 μm of the rim in the smaller two samples, with sample C experiencing this same increase- decrease zone beginning approximately 200 μm from the rim. Once again, if compared against each other on a relative scale, the compositional zoning for the garnet grains is not dependent on absolute radius, but on the relative radius of the garnet grain, with the region represented by the first 100 μm from the rim of the smaller two garnet grains being directly analogous to the first 200 μm from the rim in the larger garnet sample.

Compositional zoning with respect to XSps in all garnet samples analyzed is by far the most complex and perhaps the most informative with regard to changes in pressure, temperature, and mineral equilibrium (Banno and Chii, 1978; Săbău et al., 2006). Spessartine compositions in the garnet range from ~ 0.011 - 0.074 XSps. All XSps profiles then follow a bell-curve pattern typical of prograde metamorphism (Hollister et al., 1966; Lapen et al., 2003; Skora et al., 2006). Spessartine composition reaches its minimum 200 - 300 μm from the rim in the smaller garnet samples and 400 - 500 μm in the larger garnet samples. From this point, XSps in all garnet grains increases once more in a pattern typical of what has been identified as retrograde zoning (Gulbin, 2013). An increase of XSps towards the rim of all garnet samples is followed by a rapid rimward decrease followed by an increase in XSps towards the rim.

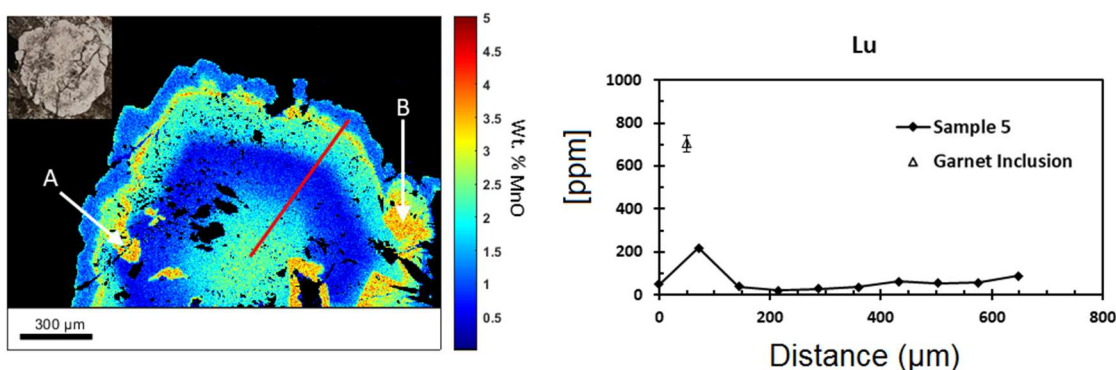


Figure 2.3: X-Ray element map of wt.% MnO for MVE12-66-1.5 (Sample 5) (left) and Lu zoning profile (right) for the same sample and marked with a red line on the X-Ray element map. This X-Ray element map appears to preserve an embayment, which is indicated at (A). Lu zoning profile is from rim to core, with garnet inclusion spot analysis taken at the uppermost inclusion indicated at (B).

The major element zoning is shown in the X-ray element map for wt.% MnO for MVE12-66-1.5 (Figure 2.3). This is particularly useful in determining the variation in composition in 2-D space, which can then be extrapolated to 3-D space. Major features to note in this X-ray element map are the decrease and initial increase of MnO follow the boundary of the original garnet grain. Meanwhile, the highest concentration of MnO ~ 100 μm from the rim roughly follows the current rim of the garnet, which is not directly parallel to the initiation of increase of MnO ~250 μm from the rim. This portion is unusual due to the presence of preserved embayments (Figure 2.3 A) as well as what appears to be small inclusions of spessartine-rich garnet within the larger garnet (Figure 2.3 B).

2.5.2: Crystal Size Distribution

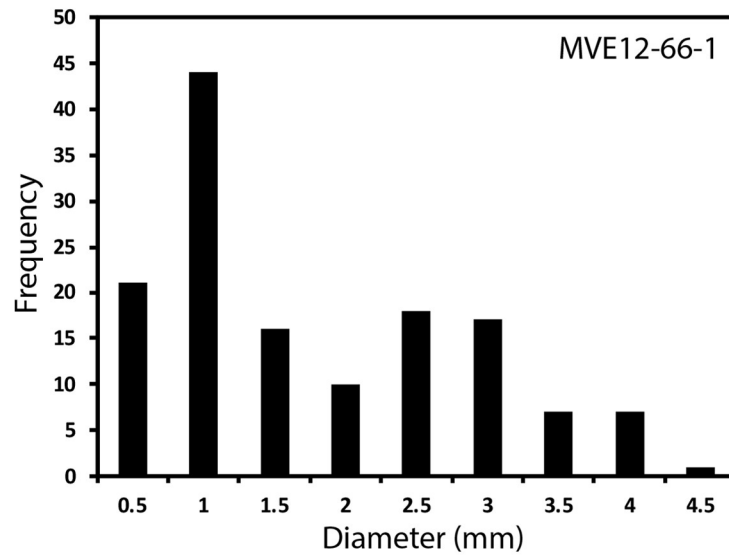


Figure 2.4: Crystal size distribution for MVE12-66-1. CSD shows an unusual bimodal distribution of garnet population, indicative of a complex growth history.

Crystal size distribution for MVE12-66-1 included measurements of 141 garnet grains in Blob3D (Figure 2.4) (Ketcham, 2005). These measurements can be useful in determining the mechanisms governing garnet growth, crystal nucleation, growth rates, and any deviations from expected growth behaviors (Cashman and Ferry, 1988; Denison and Carlson, 1997; Eberl et al., 1998; Skora et al., 2006; Cheng et al., 2008). In garnet governed by diffusion-controlled growth, the data would show a bias towards intermediate-sized grains, as diffusion halos that form around already formed garnet would suppress the formation of any further nucleation and growth of garnet surrounding the original grain, resulting in a size population of garnet biased to larger grains. If the dominant growth mechanism was interface-controlled growth, the grain size would be

biased towards a smaller grain size, as the abundance of material would allow for nucleation and growth regardless of the presence of earlier grains, resulting in a population biased towards smaller grains. (Denison and Carlson, 1997). In this sample, the crystal size distribution produced a bimodal grain size distribution.

2.5.3: Trace Element Zoning

In sample A (Figure 2.5), heavy rare earth element (HREE) concentrations are high at the core, with a rapid decrease until $\sim 200\ \mu\text{m}$ from the core, where HREE concentrations more gently decrease, as is expected for prograde-zoned garnet (Skora et al., 2006; Moore et al., 2013). At $\sim 200\ \mu\text{m}$ from the rim, there is an increase of HREEs that continues to the rim. For light rare earth elements (LREEs), there is some variability in their behavior. Sm and Nd both increase from core towards the rim, followed by a decrease in concentration that begins at a variable distance from the rim, with rim concentrations of Nd being within $\sim 0.02\ \text{ppm}$ and Sm concentrations within $1\ \text{ppm}$ between different garnet samples. This similarity between rim concentrations between garnet samples also extends to concentrations for HREEs.

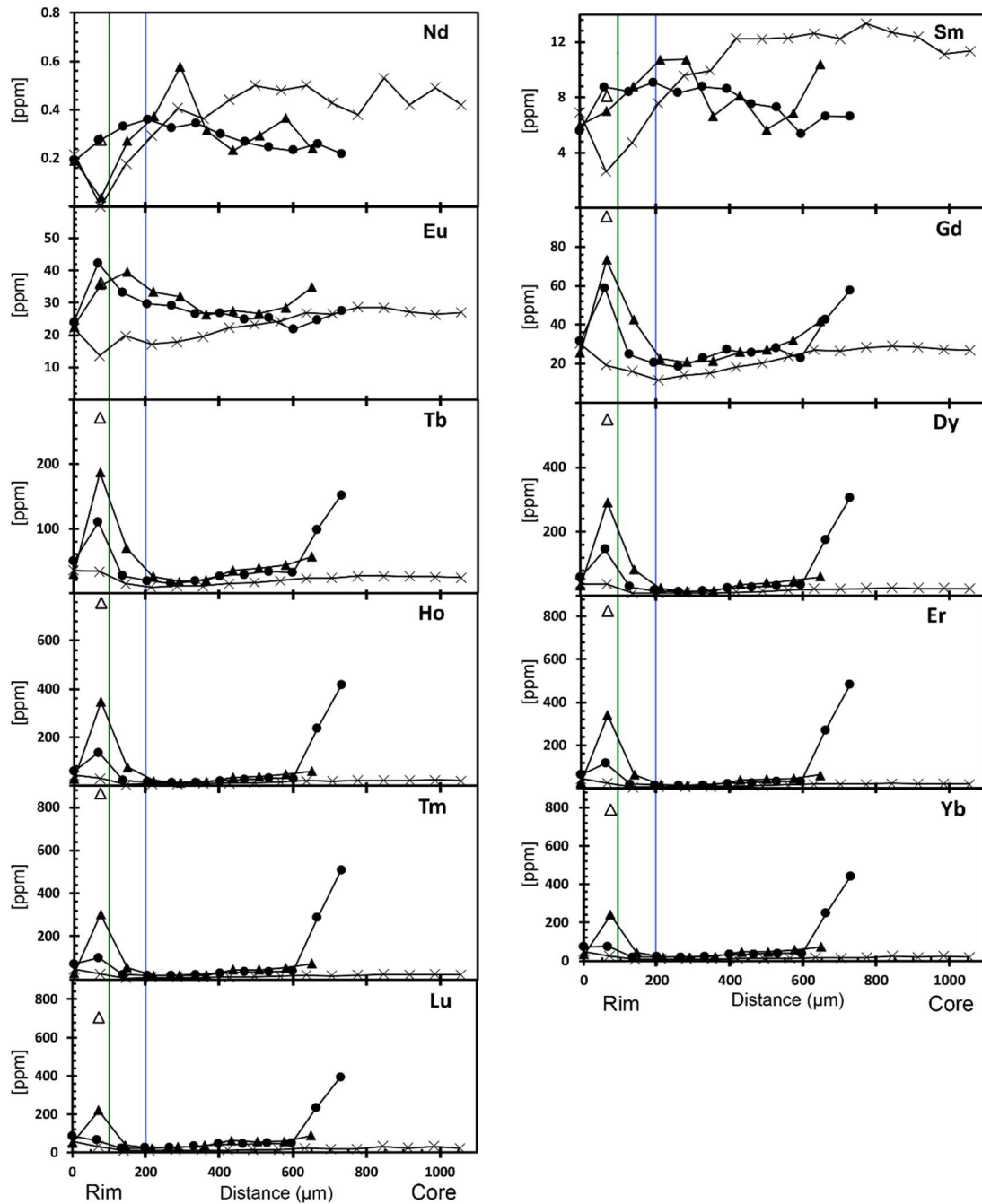


Figure 2.5: REE zoning for MVE12-66-1.4 (Sample A (Circle)), MVE12-66-1.5 (Sample 5 (triangle)), a small inclusion of garnet from Sample 5 (open triangle), and MVE12-66-4-002.1 (Sample C (cross)). Though relative concentrations vary throughout each garnet, no matter the size, the increase of REEs towards the rim begins at roughly the same distance from the rim. The blue line represents where XSps increases, and the green line represents where XSps decreases near the rim.

2.6: DISCUSSION

2.6.1: Element Zoning

Major elemental zoning data for garnet samples indicates a clear and well-defined prograde zoning pattern, as shown by a bell-shaped Mn zoning profile with decreasing Mn towards the rim, within the interior of the garnet. This zoning pattern also requires an inverse bell curve for Fe and Mg composition from core to rim, which can be subtly seen in some of the zoning profiles (Figure 2.2) (Hollister, 1966; Skora et al., 2006). This prograde chemical zoning is indicative of changes in P-T and fluid/matrix composition and is undisturbed by diffusional relaxation or re-equilibration with the matrix due to the very low temperatures experienced by these samples (Caddick et al., 2010).

The prograde zoning pattern is present from the garnet cores to about 2/3 of the radial distance toward the rims. From this distance outward, the element concentration patterns would be consistent with retrograde diffusion (i.e. increases in garnet-compatible elements such as Mn and HREE; Woodsworth, 1977; De Lima et al., 1995; Kohn and Spear, 2000; Gulbin, 2013), but retrograde diffusion is unlikely due to the very low T experienced by lawsonite eclogite. Outward from the regions rich in garnet-compatible elements, their concentrations decrease toward the rim, consistent with prograde distillation of these elements (e.g., Hollister, 1966).

In order to constrain what formed the compositional zoning up to ~200 μm from the garnet rims, it is necessary to observe the minerals present over the duration of garnet growth. Manganese and REE- rich minerals, such as epidote-group minerals, could have

broken down during prograde metamorphism and released Mn and REE to the matrix, thus increasing the overall availability of these elements during garnet growth. The lack of epidote-group minerals and the presence of lawsonite in garnet cores and matrix suggest they were not a likely source for these elements. In addition, Fe-poor epidote would participate in lawsonite-forming reactions, but lawsonite was likely stable throughout the prograde and retrograde P-T history (Tsujimori et al., 2006b; Hara et al., 2018). The most likely source of Mn is from chlorite, a mineral that participates in many garnet-forming reactions at these P-T conditions (Inui and Toriumi, 2004).

It is known that garnet growth in eclogite at lower temperatures is controlled dominantly by equilibrium with chlorite (Inui and Toriumi, 2004; Konrad-Schmolke et al., 2005). This can be seen to some extent in the garnet in this study, wherein there are inclusions of chlorite near the core of some garnet within the thin sections examined (Figure 2.1). Therefore, this increase in Mn composition midway through garnet is likely due to the continued consumption of chlorite as both garnet and chlorite coexist throughout the duration of garnet growth (Figure 2.6). Availability of Mn (and REE) to the garnet growth surface could have also been enhanced by fluids released during chlorite-consuming reactions that increased rates of intergranular element diffusion.

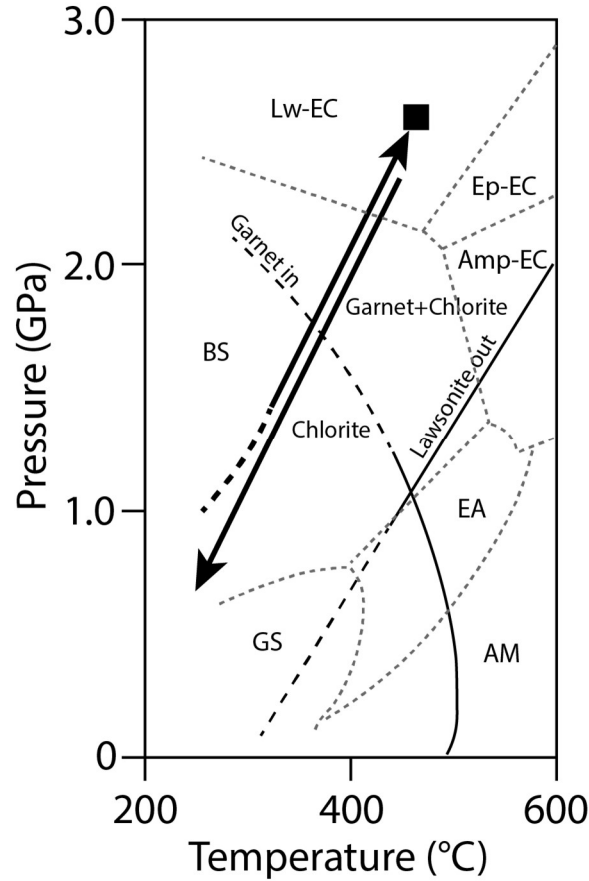


Figure 2.6: Calculated pressure-temperature (P-T) path from Tsujimori et al. 2006b, with a large square showing peak P-T conditions. Prograde path for lawsonite eclogite crosses into stability range for coexisting chlorite and garnet and remains well within lawsonite stability range. Stability range for garnet and chlorite from Inui and Toriumi (2004), lawsonite stability range from Whitney et al. (2014), dashed lines are projections of reactions. Metamorphic facies and their abbreviations are from Liou et al. (2004).

Trace element zoning for sample A (Figure 2.5) exhibits HREE zoning typical of diffusion-controlled growth of small garnet (Skora et al., 2006). However, there is a significant change in HREE concentrations at approximately $\sim 200 \mu\text{m}$ from the rim, which correlates well with the discontinuity observed at that same zone in the major element profiles. HREEs are typically sequestered in cores of garnet early during garnet growth (Skora et al., 2006; Volkova et al., 2014), which leads to the high concentrations

observed within the cores of these samples. However, the increase of HREEs at the rim is unusual, as HREEs should have already been largely sequestered within the cores of the garnet. Interestingly, a small inclusion of garnet in garnet (Figure 2.3 B; sample MVE12-66-1.5) shows Mn and HREE concentrations that are substantially higher than any other measurement taken from any garnet sample (Table 2.3), suggesting that this garnet inclusion is representative of some of the earliest garnet formed.

Table 2.1: Trace element data for lawsonite in MVE12-66-4.

Element (ppm)	Lws 1	Lws 2	Lws 3	Lws 4	Lws 5	Lws 6	Lws 7	Lws 8	Lws 9	Lws 10	Lws 11	Lws 12	Lws 13	Lws 14	Lws 15
Li	0.706	b d	b d	b d	b d	0.354	1.22	0.92	b d	b d	0.503	b d	0.504	0.369	0.294
B	2.49	1.74	b d	b d	b d	b d	0.58	b d	1.03	0.63	0.21	b d	0.37	0.3	0.72
Mg	0.015	b d	b d	b d	0.001	b d	0.02	0.001	0.005	0.002	0.012	0.001	b d	b d	b d
Sc	0.86	0.083	b d	0.061	0.172	0.108	1.758	0.157	0.215	0.135	0.41	0.124	0.039	0.034	0.12
V	6.98	5.84	4.65	7.79	5.61	8.94	6.27	4.8	6.68	6.48	9.16	8.91	11.49	3.88	5.3
Cr	0.002	0.002	b d	b d	0.011	b d	b d	0.010	b d	0.004	b d	b d	b d	0.003	b d
Co	0.004	b d	b d	b d	b d	b d	0.002	b d	b d	b d	0.002	b d	b d	b d	b d
Ni	b d	b d	b d	b d	b d	b d	b d	b d	b d	b d	b d	b d	b d	b d	b d
Cu	b d	b d	b d	b d	b d	b d	b d	b d	0.011	b d	b d	0.004	b d	b d	0.001
Sr	400.96	346.25	186.29	505.64	210.05	280.76	331.5	248.87	439.06	224.95	398.1	438.21	202.58	326.36	241.79
Y	132.29	70.04	49.75	73.38	116.56	25.41	50.76	23.41	150.12	13.06	85.75	36.22	16.08	27.68	15.46
Zr	0.27	b d	0.987	b d	0.224	b d	1.051	0.397	b d	b d	0.218	b d	0.101	0.301	b d
Nb	0.188	b d	b d	b d	b d	0.064	9.34	0.26	b d	b d	0.097	0.129	b d	0.057	b d
Mo	0.379	b d	0.88	0.532	b d	b d	0.206	b d	0.285	0.581	1.07	0.3	0.29	b d	b d
Ba	0.406	0.28	1.369	0.501	0.392	0.229	1.031	0.284	9.44	0.447	1.442	0.45	0.114	0.305	0.276

Table 2.2: REE data for lawsonite in MVE12-66-4.

Element (ppm)	Lws 1	Lws 2	Lws 3	Lws 4	Lws 5	Lws 6	Lws 7	Lws 8	Lws 9	Lws 10	Lws 11	Lws 12	Lws 13	Lws 14	Lws 15
La	355.37	86.84	84.58	268.83	227.49	122.04	152.54	44.54	395.7	31.72	183.91	75.63	28.9	102.38	52.39
Ce	372.66	108.43	107.31	359.85	311.68	156	180.45	52.04	491.51	31.71	169.72	79.82	27.91	126.56	62.41
Pr	398.22	132.58	129.14	492.82	387.65	187.84	206.07	59.94	621.9	32.8	155.8	88.92	25.85	149.58	78.13
Nd	359.7	128.01	128.59	548.5	383.17	192.07	204.03	60.33	698.59	27.47	112.47	82.69	22.55	149.75	83.25
Sm	263.04	88.81	96.93	436.59	307.98	135.91	162.1	43.68	552.44	21.91	86.46	73.19	18.28	107.48	62.3
Eu	137.67	55.84	50.49	126.23	220.96	68.88	129.51	31.5	259.92	22.12	80.26	46.64	21.32	78.54	29.33
Gd	233.35	75.77	79.51	338.87	250.3	90.78	122.49	37.65	481.54	15.19	73.85	68.09	16.41	79.78	43.13
Tb	172.51	55.32	47.06	171.53	162.84	46.49	74.01	25.08	267.17	14.15	73.16	50.51	14.92	45.37	26.45
Dy	166.74	60.56	46.5	110.62	134.47	33.53	58.95	22.64	203.13	13.21	81.29	40.07	16.35	32.04	23.46
Ho	129.96	70.03	50.91	79.16	109.87	23.73	46.91	25.86	150.46	12.16	79.95	35.31	16.1	28.1	18.78
Er	80.19	86.02	54.99	41.85	80.99	18.3	34.35	23.03	89.32	10.76	64.75	21.97	13.78	24.4	12.61
Tm	40.26	88.91	55.83	24.14	56.12	12.93	23.26	25.66	45.34	9.23	38.93	12.73	10.2	16.75	7.56
Yb	16.73	81.59	55.72	13.3	35.47	10.59	12.55	19.76	19.95	8.8	22.03	6.78	7.59	14.41	5.48
Lu	13.47	103.59	63.71	8.76	35.56	9.71	13.95	23.36	16.11	7.27	16.11	5.69	5.88	15.81	2.8
Hf	1.56	0.667	0.812	0.93	0.94	0.424	1.68	0.91	1.54	b d	0.66	b d	0.265	0.98	1.22

Table 2.3: REE data for garnet in MVE12-66-1 and MVE12-66-4.

Element (ppm)	MVE12-66-1 Sample A				MVE12-66-1 Sample 5				MVE12-66-1 Garnet Inclusion		MVE12-66-4 Sample C		
	Rim	Enriched Zone	Intermediate	Core	Rim	Enriched Zone	Intermediate	Core			Rim	Intermediate	Core
Nd	0.191	0.273	0.344	0.218	0.189	0.036	0.313	0.238	0.275		0.214	0.48	0.42
Sm	5.57	8.74	8.77	6.61	5.98	7	6.64	10.4	8.09		6.88	12.28	11.35
Eu	23.83	42.25	26.55	27.37	22.61	35.42	26.25	34.75	36.08		22.06	24.2	26.89
Gd	31.6	58.82	22.71	57.46	25.35	73.24	21.26	41.62	95.73		30.22	23.5	26.84
Tb	49.36	109.86	19.05	152.07	30.36	187.2	19.9	56.7	272.49		35.54	19.4	24.19
Dy	58.59	144.63	16.1	305.23	32.34	291.21	16.35	59.2	547.82		38.95	18.17	23.26
Ho	60.35	136.87	13.83	419.23	28.18	347.22	15.63	60.46	756.95		42.77	16.55	20.8
Er	63.9	117.13	16.52	484.08	28.22	342.01	15.4	62.53	828.51		45.38	15.47	20.12
Tm	71.33	100.21	20.96	507.54	28.79	302.87	19.21	72.16	864.93		46.28	14.01	20.49
Yb	73.17	75.82	24.11	440.48	33.82	241.25	23.33	72.61	787.39		48.83	13.17	19.26
Lu	85.2	63.88	31.65	392.56	48	219.52	36.14	87.35	704.6		58.74	14.37	22.84

Sr zoning in garnet could be indicative of processes going on at depth with regards to changes in trace element budget due to the introduction of new material through fluid infiltration and/or through mineral reactions. Sr is preferentially incorporated into lawsonite (Table 2.1) (Usui et al., 2007; Martin et al., 2014; Vitale Brovarone et al., 2014; Fornash et al., 2019). Therefore, if garnet is either growing during or after lawsonite formation, the concentration of Sr across the garnet should reflect this. Hara et al. (2018) predicted a second generation of lawsonite formation that occurred after peak P-T conditions for lawsonite eclogite from the southern mélangé in the Guatemalan suture zone. If this were the case, one would expect the concentration of Sr to be lower in portions of garnet that grew after the formation of secondary lawsonite. The concentration of Sr across garnet sample MVE12-66-1.5 (Figure 2.7) and the composition of the small garnet inclusion show a decrease of Sr across the inclusion-free rim of the garnet. Sr zoning in sample A from the same eclogite sample has a zoning profile that is less obscured by inclusions, with an increase towards the rim, but a decrease at the rim, similar to patterns of REE and Mn.

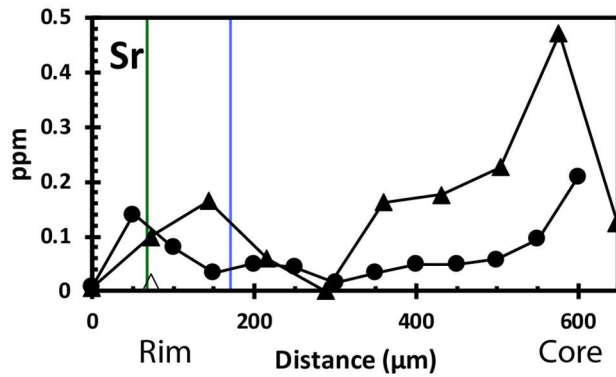


Figure 2.7: Sr concentration across garnet. Due to its substantial compatibility in lawsonite, Sr concentration in garnet may be used to determine if lawsonite is either being consumed or is forming during garnet growth. The blue line represents where XSps increases, and the green line represents where XSps decreases near the rim.

2.6.2: Crystal Size Distribution

The crystal size distribution (CSD) produced for MVE12-66-1 is rather unusual due to the presence of a bimodal distribution of grain size for garnet. CSD for garnet will typically either be weighted towards smaller grain sizes in interface-controlled growth or to more intermediate grain sizes in diffusion-controlled growth (Denison and Carlson, 1997; Eberl et al., 1998). If Ostwald ripening were at work, then one would expect the peak to be shifted towards larger grains (Cashman and Ferry, 1988; Miyazaki, 1991; Cheng et al., 2008). The presence of two peak populations suggests that there may be more than one dominant growth mechanism at work at different times.

2.6.3: Evidence for Multi-stage Growth

The abrupt change in major element zoning, as well as the increase in HREE concentration by up to ~ 275 ppm for some HREEs within ~200 μm from garnet rims, indicates that the inclusion-free rim of garnet represents a second garnet growth (overgrowth) and nucleation episode (De Lima et al., 1995; Raimbourg et al., 2007;

Konrad-Schmolke et al., 2008). This is supported by the bimodal CSD, which would be possible if pre-existing garnet were to be enlarged at the same time new, smaller garnet grains were also nucleating. Smaller garnet populations that are particularly rich in garnet-compatible elements, but only preserved as garnet inclusions (Figure 2.3 B) are found in the same region of garnet that preserved a gradual increase in Mn concentration and initiation of increase of HREEs, the availability of garnet-compatible elements to the growing garnet interface and the increased rate of garnet nucleation requires enhanced availability of garnet-forming components. Fluid-enhanced element mobility could be a mechanism for the new garnet and availability of garnet-compatible elements with the introduction of a hydrous component during prograde metamorphism, which has been observed by Hara et al. (2018). Increased supply of garnet-forming components, either through fluid enhanced intergranular diffusion and/or by consumption of a mineral phase, such as chlorite, would then result in increased garnet nucleation and growth, which can be seen in the presence of small garnet inclusions in garnet (Figure 2.3 B) as well as the bimodal distribution in garnet grain size (Figure 2.4) (Inui and Toriumi, 2004; Gardés et al., 2012).

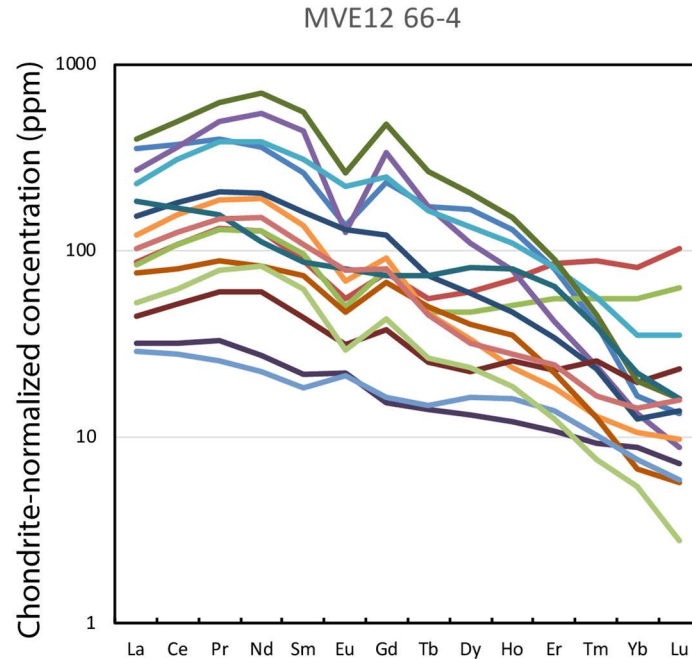


Figure 2.8: REE composition of lawsonite inclusions in garnet in MVE12-66-4. All lawsonite samples observed contained an abundance of LREEs, with a lower concentration in HREEs.

Sr and LREE zoning also lend evidence for a multi-stage growth for garnet. Since Sr and LREEs are preferentially incorporated into lawsonite (Figure 2.8; Tables 2.1 and 2.2) (Usui et al., 2007; Martin et al., 2014; Fornash et al., 2019), the decrease or increase of these elements in garnet would be indicative of the gain or loss of lawsonite in the matrix, respectively. In these samples, I see a decrease of Sr and LREEs in garnet towards this rim (Figures 2.5 and 2.7; Table 2.4), with a significant decrease of these elements at the rim within the inclusion-free zone that has been identified as a secondary growth zone. Therefore, since there is a decrease in these elements at this point, it suggests that there must have been an introduction of a secondary generation of lawsonite, as has been observed by Hara et al. (2018), which would serve as a reservoir

for these elements, sequestering them from incorporation into garnet during a second growth generation. It is possible, then, that this secondary generation of garnet grew after the formation of secondary lawsonite.

Table 2.4: Trace element data for two garnet zones in MVE12-66-1

	Sample A				Sample 5				Garnet Inclusion
Element (ppm)	Rim	Enriched Zone	Intermediate	Core	Rim	Enriched Zone	Intermediate	Core	
Li	0.698	0.646	0.445	0.742	b d	0.71	0.274	0.71	0.94
B	b d	1.64	b d	0.6	1.56	1.5	0.77	b d	0.94
Sc	7.74	4.01	9.07	6.59	9.92	4.79	8.92	9.65	7.3
V	0.784	0.849	0.649	0.968	0.462	0.845	0.823	0.865	1.064
Cr	0.013	0.004	0.002	b d	0.004	0.005	0.002	0.003	0.017
Co	0.054	0.047	0.041	0.03	0.075	0.04	0.041	0.035	0.037
Ni	b d	b d	b d	b d	b d	b d	b d	b d	b d
Cu	0.007	0.007	0.024	0.015	0.007	0.01	b d	b d	0.008
Sr	0.009	0.140	0.016	0.209	0.007	0.099	0.162	0.126	0.016
Y	354.82	177.58	15.88	31.7	30.15	374.02	15.5	57.47	723.89
Zr	0.224	2.83	3.87	0.41	0.316	0.145	0.414	0.398	0.163
Nb	0.044	b d	b d	0.208	0.061	b d	b d	0.214	b d
Mo	2.36	1.94	0.571	0.95	0.202	0.927	0.315	0.548	1.27
Ba	b d	0.030	0.006	0.095	0.015	0.022	0.126	b d	0.092
La	b d	b d	b d	b d	b d	0.057	0.0245	b d	0.021
Ce	0.01	0.006	0.007	0.024	b d	b d	0.007	0.018	b d
Pr	b d	0.045	0.015	0.022	0.047	0.065	0.079	0.025	0.138

Based on the combination of major and REE zoning, I interpret that initial garnet nucleation and growth was facilitated by the consumption of chlorite, which is present in both prograde and retrograde assemblages (Figure 2.9). As garnet growth continued, Mn concentration began to increase ~250 μm from the rim, due to increased intergranular diffusion during the consumption of hydrous phases and release of hydrous material into the system (Gardés et al., 2012), which allowed more Mn to reach pre-existing garnet as well as enhancing garnet growth and nucleation of new garnet grains. The hydrous phase consumed is likely lawsonite, as is reflected in the increase in concentration of Sr and LREEs observed beginning ~250 μm from the rim. After the formation of a second

generation of lawsonite (Hara et al., 2018), garnet growth of the inclusion-free garnet rims likely formed through continued consumption of omphacite, phengite, and lawsonite, resulting in the formation of both garnet and the lens-shaped quartz found in the matrix. The decrease of Mn and HREEs at the rim is interpreted to be due to normal prograde distillation of garnet-compatible elements after a period of fluid-enhanced intergranular diffusion.

	Metamorphic Stage	Prograde I: Normal Zoning	Prograde II: Oscillatory Zoning	Matrix
Type I Lawsonite Eclogite	Garnet			
	Omphacite			
	Lawsonite			
	Phengite			
	Chlorite			
	Quartz			
	Albite			
	Rutile			
	Ilmenite			
	Titanite			

Figure 2.9: Mineral paragenesis for Type I lawsonite eclogite. Most major garnet-forming minerals were present throughout the prograde and retrograde history, allowing for multiple stages of garnet growth. Diagram modified from Tsujimori et al., 2006b.

2.7: IMPLICATIONS

Garnet serves as a valuable indicator for a variety of processes going on during subduction and exhumation with regards to changes in pressure, temperature, and fluid interactions. Combining major, trace and REE profiles with crystal size distribution and X-ray element maps, I can create a more complete picture of how these changes can affect garnet composition as well as its relationship with accessory mineral phases. In this case, the relationship between garnet and lawsonite serves as an indicator of fluid

mobility during subduction, as well as changes in nutrient availability due to introduction of new materials during pulses of hydration and increased intergranular diffusion. X-ray element maps for garnet also allows for the identification of inclusions of small garnet into larger garnet that would not be apparent from major element profiles alone, allowing for the identification of changes in conditions of garnet growth, such as an increase in garnet-compatible elements allowing for increased garnet nucleation and growth after the timing of initial garnet nucleation. The bimodal crystal size distribution, too, also serves as a valuable piece of evidence of a complex metamorphic history, which is punctuated by multiple garnet nucleation events. Using these techniques in other HP/LT subduction complexes may also reveal a more complex history than was originally assumed and could be employed to resolve inconsistencies between data sets between metamorphic assemblages across a region.

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Chapter 3: COMPLEX ZONING MAY REFLECT A SIMPLE SUBDUCTION HISTORY

3.1: INTRODUCTION

Geochemical and petrological analyses of metamorphic assemblages have been traditionally used in order to give insight into the prograde and retrograde history of a metamorphic rock. The most commonly used mineral for these analyses is garnet, considered to be the most robust and useful due to its ability to record discrete changes in chemical composition in response to changes in pressure and temperature throughout the duration of garnet growth (e.g., Bollingberg and Bryhni, 1972; Mezger et al., 1992; Schumacher et al., 1999; Skora et al., 2006; Carlson, 2012). These changes can result in complex chemical zoning patterns in garnet, which can be difficult to interpret, and have been used to develop complex P-T histories for subduction zones around the world (Figure 4) (e.g., Blanco-Quintero et al., 2011; Garcia-Casco et al., 2002). These complex histories can include events such as: fluid infiltration (e.g., Jamtveit et al., 1995; Stowell et al., 1996; Ivanova et al., 1998; Meth and Carlson, 2005; Konrad-Schmolke et al., 2014), pulsed garnet growth (De Lima et al., 1995; Săbău et al., 2006; Zhou et al., 2011; Zhou et al., 2014), and poly-cyclic subduction (e.g., Garcia-Casco et al., 2002; Brueckner, 2006; Rubatto et al., 2011). There are, however, instances wherein the P-T history of a subduction zone is already well defined as a simple subduction and exhumation history while still having a complex chemical zoning present within their garnet (Tsujimori et al., 2006b). Herein, I shall explore how complex chemical zoning within a garnet can form using a simple growth history.

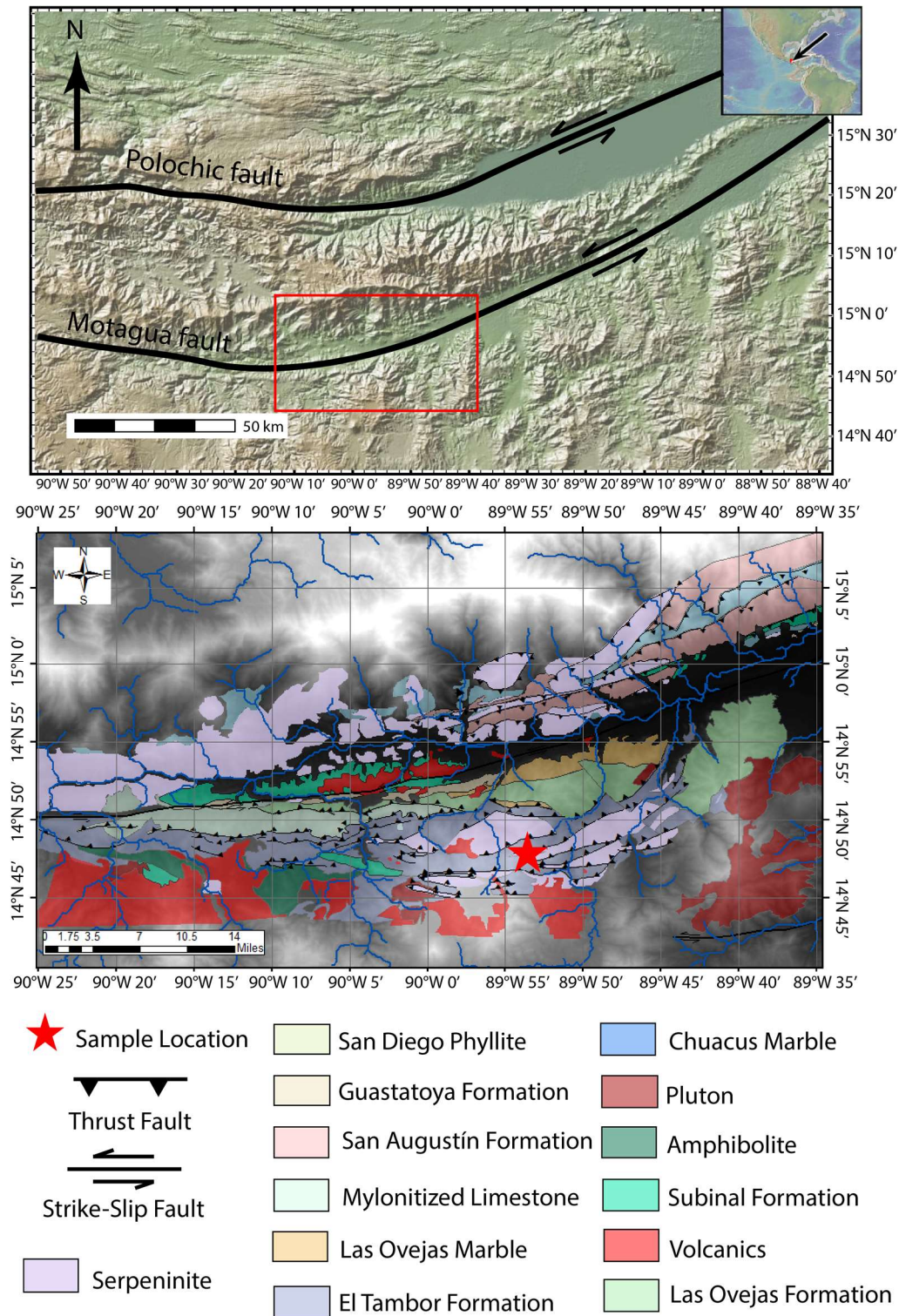


Figure 3.1: Map of the Motagua Suture Zone. Geologic map reproduced from unpublished map by Sisson (personal communication 2014).

Lawsonite eclogites sourced from the southern serpentinite mélangé from the Guatemalan suture zone in central Guatemala (Figure 3.1) have a calculated P-T history that starts with the initiation of eclogitization at 1.1 GPa and 300 °C, proceeding to peak conditions of 2.6 GPa and 480 °C (Tsuji-mori et al., 2006b). This prograde history is then followed by a swift exhumation that allowed the preservation of lawsonite within the eclogite samples (Harlow et al., 2004; Tsuji-mori et al., 2006a; Tsuji-mori et al., 2006b; Brueckner et al., 2009). With such a straightforward history, one would expect that the garnet chemical zoning would also be simple. However, garnet from these lawsonite eclogites have been observed to have oscillatory zoning in Mn composition (Tsuji-mori et al., 2006a), along with other complex zoning features, such as embayments or secondary garnet as inclusions within a main host garnet. Additionally, garnet from these eclogites have an unusual heavy rare earth element zoning that deviates from the expected pattern for garnet, with an increase of HREEs at the rim of the garnet.

In order to resolve this difference between the chemical zoning of the garnet and the P-T history of the lawsonite eclogite, I modeled heavy rare earth element zoning in garnet for this range of temperatures and composition over a continuous growth history, comparing different growth-rate limiting models for garnet growth and nucleation. Using these models, I am able to reproduce the HREE zoning observed under these conditions. These models show that, regardless of growth-rate model used, there will be a secondary increase of HREEs at the rim of the garnet, indicating garnet grew continuously during these P-T conditions. In fact, it is because of these P-T conditions that garnet can produce such complex and unexpected zoning patterns.

3.2: GEOLOGICAL SETTING

The Guatemala suture zone in central Guatemala serves as the boundary between the Maya block of the North American plate to the north and the Chortís block of the Caribbean plate to the south (Figure 3.1) (e.g., Flores et al., 2013). A unique feature of this suture zone is that it contains two belts of serpentinite mélangé that contain smaller blocks of high pressure, low temperature rocks (Harlow et al., 2004; Flores et al., 2013). Sm-Nd dating of eclogites from both sides of the fault reveal timing of formation for these metamorphic rocks to have occurred between 140 and 120 Ma, which has been interpreted to mean that the serpentinite mélanges on both sides of the fault originated from the same tectonic event (Brueckner et al., 2009). Though this is indicative of a shared history, this is where their genetic similarity ends. Phengite $^{40}\text{Ar}/^{39}\text{Ar}$ ages for jadeitite, eclogite and other assemblages differ on either side of the fault, with northern ages ranging 77-65 Ma and southern ages ranging 125-113 Ma, it is clear that an additional tectonic event occurred in the north that was not recorded in the south (Harlow et al., 2004; Brueckner et al., 2009; Flores et al., 2013).

While the mélangé to the south of the Motagua fault would appear at first to be the more straightforward of the two serpentinite belts with the lack of overprinting that was recorded to the north of the fault, the geochemical analyses of lawsonite eclogite samples from this region indicate that this previously-thought simple prograde and retrograde history may be significantly more complex than initially anticipated, with recent research indicating the presence of secondary, post-peak P-T periods of garnet and lawsonite growth (Hara et al., 2018).

3.3: METHODS

Rare earth element analyses were performed using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the University of Houston. LA-ICP-MS equipment consisted of a Photon Machines Analyte.193 laser ablation instrument coupled to a Varian 810-MS quadrupole ICP-MS. Trace element and REE analysis includes: ^7Li , ^{11}B , ^{25}Mg , ^{29}Si , ^{29}Sc , ^{51}V , ^{52}Cr , ^{55}Mn , ^{59}Co , ^{88}Sr , ^{89}Y , ^{91}Zr , ^{93}Nb , ^{95}Mo , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{149}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{173}Yb , ^{175}Lu , and ^{178}Hf . Laser sampling was conducted with a laser frequency of 10 Hz with a spot size of 50 μm . Data acquisition alternated between two standard analyses and four “unknown” garnet sample analyses, with each analysis preceded by a gas blank of approximately 18s. All trace element data was corrected for laser and ICP-MS element fractionation using USGS external standard BHVO-2G glass as isotopic standard with magnesium values used for normalization collected from corresponding electron microprobe analysis using the commercial data reduction software Glitter.

Rare earth element modeling was conducted for Lu concentrations in garnet from MVE12-66-1.4. These models were used to attempt to determine the mechanism for a reproducible increase of Lu at the rim of garnet from different eclogite samples. MVE12-66-1.4 was chosen due to it being the only REE profile gathered that had a central peak in Lu concentration. Models were calculated over two separate ranges of temperatures that were taken from two separate P-T models for southern Motagua eclogites, one being 300-480 $^{\circ}\text{C}$ (Tsuji-mori et al., 2006b) and the other being 470-520 $^{\circ}\text{C}$ (Endo et al., 2012). Calculations were done in MATLAB following the program and instructions as provided

in Hesse (2012). The value for time (t) used to serve as a length of time allowed for garnet growth is 2×10^7 year (Brueckner et al., 2009) and is used in the calculations directly affecting growth rate, where interface-controlled growth invokes a linear growth rate over time and diffusion-controlled growth invokes a square-root of time growth rate. There were three different ranges for radius for diffusion that were used in these calculations: one at 0.1 cm, one at 0.2 cm, and another at 0.3 cm to determine the affect of the radius of diffusion through the matrix to the nucleation point would have on the profile generated. Radius of the garnet produced by this model was 0.076 cm. The partition coefficient (K_D) for Lu was determined using the formula $K_D = c_{grt}^{Lu} / c_m^{Lu}$, which was determined to be 243.43. The initial concentration of garnet used was 450 ppm, estimated from the highest value from MVE12-66-1.4. The concentration of Lu in the matrix was taken from Sorensen et al. (2009) with a value of 1.8 ppm. The values for Q and D_0 were taken from Skora et al. (2006), being 180 kJ/mol and 2.8×10^5 cm²/yr, respectively.

X-ray element maps for Si, Ti, Al, Mg, Mn, Ca, Fe, K, Na, and Ba were collected simultaneously using the Cameca SX100 electron microprobe at the American Museum of Natural History. Collection conditions for these analyses included a beam current of approximately 80 nA, an accelerating voltage of 15 kV, a dwell time of 85 ms, a beam diameter of 1 μ m, with a step size of 3 μ m. Additional profile and spot analyses were collected at the same time for use in creating quantitative X-ray element maps in XMapTools version 2.1.7 (Lanari et al., 2014).

3.4: RESULTS

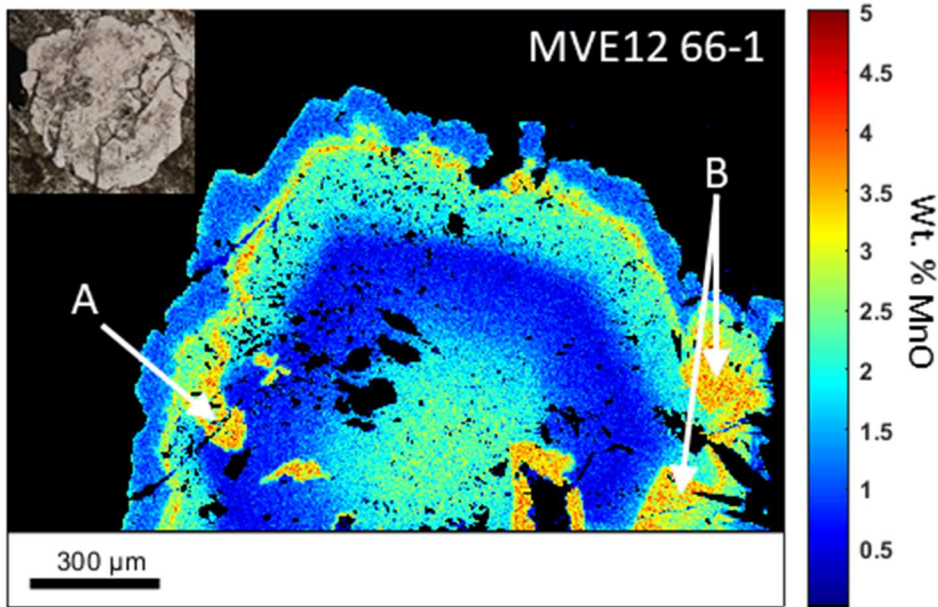


Figure 3.2: X-ray element map for MnO for a garnet sample from MVE12-66-1. This element map displays core peak of Mn, with secondary maxima approximately 100 μm from the rim of the garnet. Other features of more are A) a preserved embayment and B) small garnet inclusions in the host garnet.

X-ray element maps of Mg, Ca, Fe, and Mn (Figure 3.2) are not typical for prograde garnet zoning (Hollister et al., 1966; Săbău et al., 2006). Rather than the expected pattern for Mn, Mn instead has an initial bell-shaped curve that is disrupted halfway through the garnet radius by a steady increase in concentration of Mn that proceeds towards the rim, marked by a significant increase of Mn approximately 100 μm from the rim, with an abrupt decrease after this increase. Additionally, the Mn maxima near the rim of garnet follows closely with grain boundaries but deviate in several locations and also highlight unusual rectangular maxima near the garnet rim. Fe also has a marked decrease at approximately 100 μm , showing an inverse relationship with Mn.

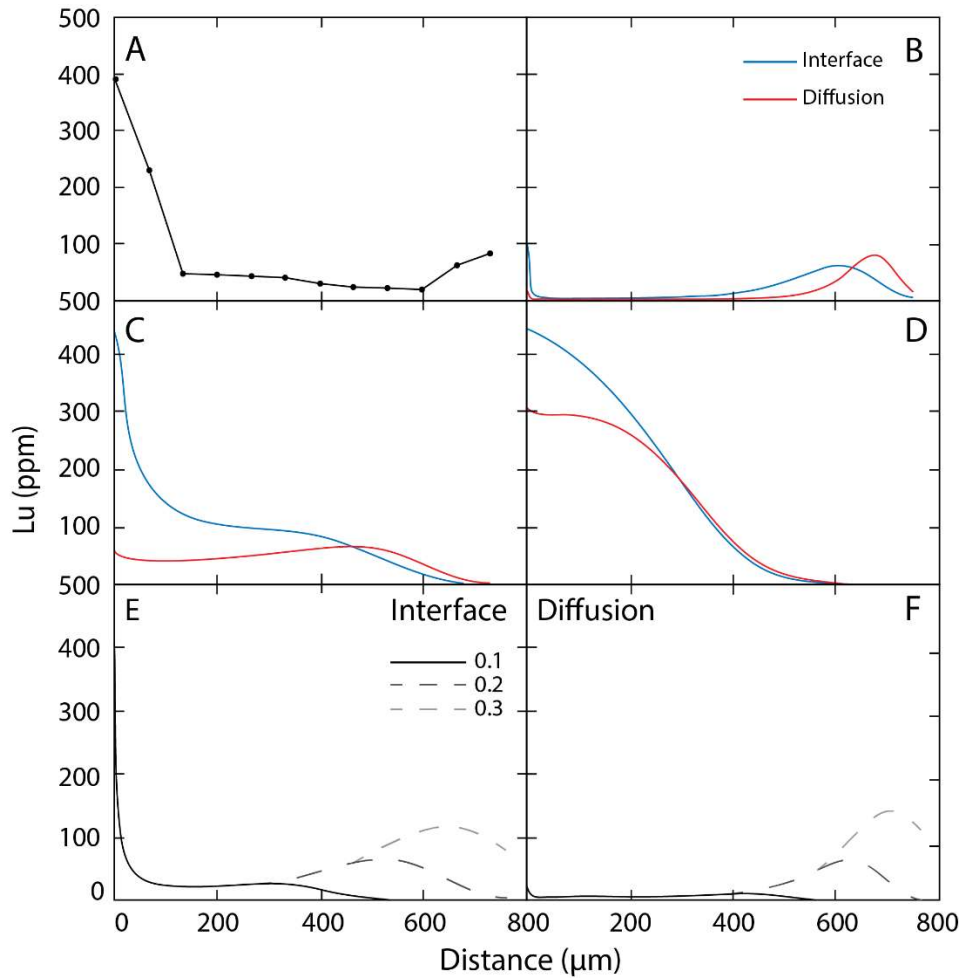


Figure 3.3: Chemical zoning profiles for Lu. A) Measured data for Lu for MVE12-66-1. Modeled chemical zoning profiles for B) 300-480°C, C) 400-480°C, D) 470-520°C. Comparison of different chemical zoning profiles for E) interface-controlled growth and F) diffusion-controlled growth at different diffusion radii (cm).

Heavy Rare Earth Element (HREE) analysis of garnet samples produced zoning patterns that are largely typical of prograde growth (e.g., Lapen et al., 2003; Skora et al., 2006). These elements, which include Lu (Figure 3.3 A), Yb, and other HREEs have higher concentrations in the garnet core, with an abrupt decrease outward from the core. What makes these zoning profiles unusual is the subsequent increase of these elements beginning approximately 100 μm from the rim of the garnet.

In order to model these unusual HREE zoning profiles, I followed the methods used by Hesse (2012) and Skora et al., 2006 for Lu. Input parameters used for all of these calculations included a duration of garnet growth of 2×10^7 years (Brueckner et al., 2009), a pre-exponential diffusion factor (D_0) of $2.8 \times 10^5 \text{ cm}^2/\text{year}$ (Skora et al., 2006), and equilibrium partition coefficient (K_D) of 529.73. For each variation in radius of the diffusion domain (r) and temperature path (T), I also modeled two different possible growth mechanisms for garnet growth. These two models are interface-controlled growth, modeled using a linear growth rate over time, and diffusion-controlled growth, which was modeled using a square root of time growth rate.

Initial models were calculated using the temperature history determined by Tsujimori et al. (2006) with initiation of garnet growth occurring at 300 °C and ending at 480 °C and used a radius of the diffusion domain from the nucleation point of 0.2 cm (Figure 3.3 B). The profiles produced from these calculations have a couple of small differences. The profile produced by interface-controlled growth under these conditions shows high concentrations of Lu at the core that quickly decreases outward from the core, with a subsequent gradual increase towards the rim of the modeled garnet that begins at approximately 0.025 cm from the core and peaks at approximately 0.06 cm from the core and decreases once more. The diffusion controlled garnet profile had lower concentrations of Lu at the core, but an increase of Lu towards the rim that initiates approximately 0.04 cm from the core and peaks at approximately .068 cm from the core.

In order to reproduce the core increase of Lu observed in my data, I increased the initial temperature of garnet growth to 400 °C and stopped garnet growth at 480 °C,

while maintaining the radius of the diffusion domain used in the previous model (Figure 3.3 C). In this model, the profile produced by interface-controlled growth had a core with a high concentration of Lu, with a gradual decrease in Lu that plateaus before decreasing further towards the rim. The profile produced from diffusion-controlled growth again had little in the way of high concentrations at the core of the garnet but did produce an increase of Lu towards the rim of the garnet that peaked at approximately 0.05 cm from the core of the garnet.

I also used the temperature history calculated by Endo et al. (2012), which had garnet growth initiating at 470 °C and ending at 520 °C, with the radius of the diffusion domain remaining at 0.2 cm (Figure 3.3 D). For these parameters, both interface and diffusion-controlled growth produced high concentrations of Lu in the cores of the garnets with a gradual decrease in Lu towards the rim.

A final temperature path was calculated from 350-480 °C (Figure 3.3 E, F), serving as an intermediate model between the first two models. In this instance, interface-controlled growth (Figure 3.3 E) once again produced high concentrations of Lu in the core of the garnet that rapidly decreased outward from the core but began to increase once more beginning approximately 0.028 cm from the core and peaking at approximately 0.055 cm from the core before decreasing once more. Diffusion controlled growth (Figure 3.3 F) also had low concentrations of Lu in the core of the garnet but did have an increase towards the rim that peaked at approximately 0.068 cm from the core of the garnet.

The temperature path used in this last model was also used in determining the effect that differences in the radius of the diffusion domain from the nucleation point has on the profile produced in the two different growth models. In both models, a change in the diffusion domain radius had no effect on the core concentration of Lu. However, in both interface and diffusion-controlled growth, an increase in the radius in the diffusion domain also resulted in a shift in the secondary maximum of Lu towards the rim, as well as an increase in the concentration of Lu experienced at the peak of this secondary peak of Lu.

3.5: DISCUSSION

The complexity of the chemical zoning found within garnet can be seen in simple concentration profile analyses across the garnet grains, but it is the X-ray element maps that document the full complexity of chemical zoning in garnet from these lawsonite eclogites (Figure 3.2). This complexity is best seen in the concentration map produced for Mn, which shows the greatest difference from expected prograde chemical zoning (Hollister et al., 1966; Schumacher et al., 1999; Săbău et al., 2006). In this elemental map there is evidence of embayments preserved in the high-Mn line that runs roughly parallel to the rim of garnet. In addition, there also are rectangular-shaped regions that show an increase of Mn that take on the appearance of inclusions but are a continuous part of the garnet. There are many possible explanations for these features, for one, the zoning may be caused by resorption processes as seen in pelitic garnets (Kohn and Spear, 2000), which would also explain the embayments that occur close to the rim of garnet. The portion of garnet found after this point would then be attributed to a later stage of garnet growth (e.g., De Lima et al., 1994; Garcia Casco et al., 2002; Raimbourg et al., 2007;

Konrad-Schmolke et al., 2008). Additionally, the rectangular areas with a high Mn concentration could be explained as smaller, Mn-rich garnets that were included into the larger host garnet during growth (e.g., Săbău et al., 2006) and would suggest that, due to their close proximity and increase of Mn, garnet growth was dominated by interface-limited growth (Skora et al., 2006).

Beyond their complexity in major element zoning, garnet also has unusual HREE zoning. While the garnet samples have the expected central peak in HREEs (Lapen et al., 2003; Skora et al., 2006), there is an additional increase of HREEs at the rim of garnet (Figure 3.3 A). This spike of HREEs at the rim could potentially be explained using a complex P-T history that involves multiple subduction and exhumation events (Figure 3.4), or through infiltration of fluids containing a high concentration of HREEs into the host eclogite, or even through different growth rate limiting mechanisms working on the garnet. In order to understand this chemical zoning, Lu serves as an excellent marker for garnet growth and its history due to its compatibility in garnet as well as its slow to negligible diffusion rate at the temperatures experienced.

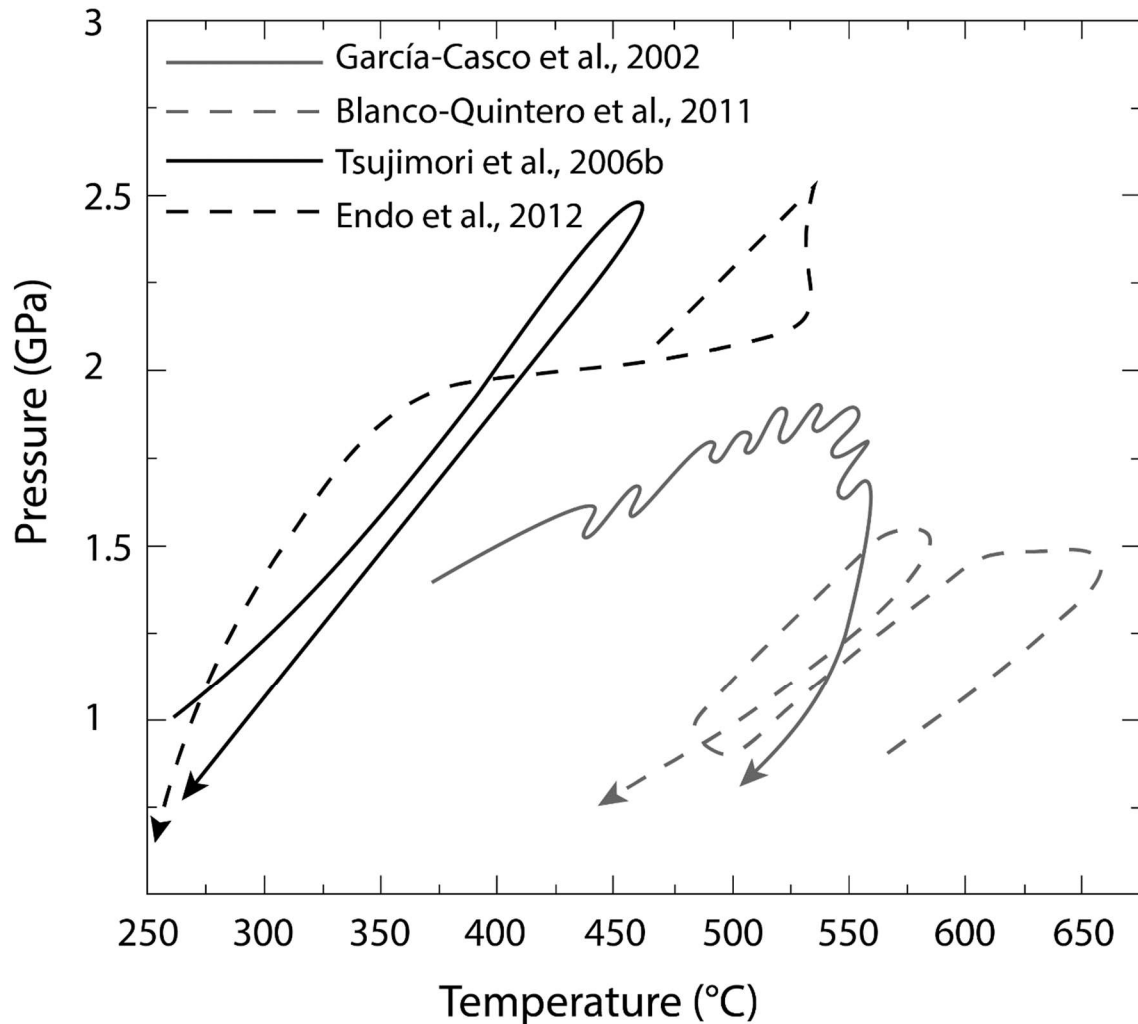


Figure 3.4: Comparison of four different P-T paths calculated for various samples with complex chemical zoning in garnet.

Calculated models for the zoning of Lu show that temperature can have a significant effect on the profile generated. The initial models (Figure 3.3 B) show that the temperature range of 300-480 °C calculated by Tsujimori et al. (2006) fails to produce a central peak in Lu for both interface and diffusion-controlled growth, but both growth mechanisms result in an increase of Lu towards the rim. Increasing the starting temperature to 400 °C (Figure 3.3 C) gives a, broad, central peak in Lu for interface-

controlled growth without a secondary increase at the rim and a very small central peak in Lu for diffusion-controlled growth with the secondary increase of Lu preserved at the rim. Increasing the temperature further to those calculated by Endo et al. (2012) (Figure 3.3 D) result in broad central peaks in Lu for both growth mechanisms but fail to reproduce the secondary peak at the rim from our measured data. These models indicate that, while the peak temperature can influence the chemical zoning of the garnet, it is the temperature experienced at nucleation that dictates whether the expected central peak is produced as well as the secondary increase at the rim. These models also show that it is unnecessary to create complex models to generate complex chemical zoning in garnet.

In addition to the effect that temperature and growth mechanism have on the chemical zoning profile produced in these models, the radius of the diffusion domain from the nucleation point into the matrix also makes a notable difference. As the radius of the diffusion domain increases, the location of the secondary maximum of Lu moves toward the rim.

Comparing the calculated profiles to the measured data shows that no model can exactly replicate the observed chemical zoning. In none of the models is diffusion-controlled growth able to completely reproduce the expected core and rim high concentration of Lu in the same model. In addition, interface-controlled growth is unable to produce the secondary increase at the rim at higher temperatures. In all cases, a cooler starting temperature is required to produce an increase of Lu at the rim, regardless if there is a high concentration of Lu at the core.

If the increase at the rim did not exist, then the modeled profile using interface-controlled growth would most accurately reflect the measured data. As there is the secondary peak at the rim, an additional mechanism is required. Though interface-controlled growth best reproduces the core zoning, the secondary increase begins much too far from the rim and does not reflect the abrupt increase that can be seen in the measured data. Diffusion-controlled growth, however, does better reproduce the abrupt increase at the rim, but fails to reproduce the core concentration required.

In determining potential growth mechanisms for garnet growth only one growth mechanism is usually considered (e.g., Meth and Carlson, 2005; Skora et al., 2006), but it is very likely that these two growth mechanisms are both operative and alternate which is the dominant growth mechanism. Early garnet growth would be dominated by interface-controlled growth where early growth is able to proceed easily due to the abundance of materials. Later, as material becomes scarce, diffusion-controlled growth would take over as the dominant growth mechanism, as nutrients would come from further away in the matrix, an effort that would be aided by thermally activated diffusion as temperature increases (e.g., Spear, 2014).

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Chapter 4: VARIABILITY OF MAJOR AND TRACE ELEMENT ZONING FOR GARNET IN DIFFERENT LAWSONITE ECLOGITE SAMPLES FROM THE GUATEMALAN SUTURE ZONE SUGGESTS UNIQUE P-T HISTORY BETWEEN ECLOGITE SAMPLES

4.1: INTRODUCTION

Garnet is a particularly useful mineral in determining processes going on during prograde and retrograde metamorphism due to its sensitivity to changes in 1) pressure, 2) temperature, 3) bulk composition, and 4) nutrient availability (Spear, 1993, Moore et al., 2013). Due to the low diffusivity of major and trace elements through garnet at low temperatures (Caddick et al., 2010), garnet from metamorphic facies that experienced low temperature (LT)/ high pressure (HP) metamorphism will record changes in these four parameters throughout garnet growth as changes in major and trace element composition across garnet, showing up as discrete chemical zoning (e.g., Lapen et al., 2003; Faryad and Chakraborty, 2005; Skora et al., 2006; 2015; Kim, 2006; Raimbourg et al., 2007; Konrad-Schmolke et al., 2007; Kohn, 2009; Zhou et al., 2011; Zhang et al., 2017).

Garnet that displays an unusual zoning in major and trace element concentrations is often attributed to a complex P-T history that may include garnet growth during the retrograde path (e.g., Hoscheck, 2001; Ota et al., 2004; Tsujimori et al., 2006b), or multiple prograde paths (e.g., LeBayon et al., 2006; Kabir et al., 2010; Blanco-Quintero et al., 2011; Herwartz et al., 2011; Regis et al., 2014; Cheng et al., 2016; Li et al., 2016; Liati et al., 2016). However, in locations with a calculated P-T history that precludes

these complex P-T trajectories, the only remaining parameters controlling garnet composition are bulk composition and nutrient availability.

In complexly zoned garnets, it becomes both a challenge and a necessity to provide constraints on the timing of garnet growth to tie changes in these four parameters to points in time in the evolution of a subduction zone (Scherer et al., 2000; Dragovic et al., 2015; Cheng et al., 2016). In dating garnet, there are several options to choose from, including: Sm-Nd, Rb-Sr, or Lu-Hf (e.g., Christensen et al., 1989; Vance and O’Nions, 1992; Kylander-Clark et al., 2007; Kohn, 2009; Pollington and Baxter, 2010; Dragovic et al., 2012). Using a combination of Lu-Hf and Sm-Nd can constrain the timing of both early garnet growth and late garnet growth (Lapen et al., 2003) but can be difficult if there is insufficient concentrations of any end member.

Lawsonite eclogite from the South Motagua Suture Zone represents one of the coldest subduction zones in the world (Harlow et al., 2004; Tsujimori et al., 2006a; Tsujimori et al., 2006b; Harlow et al., 2011). Due to the cold temperatures experienced by these eclogites, any garnet that grew is representative of localized equilibrium with the matrix that changes as garnet grows and matrix compositions evolve. There are two competing models for the P-T history for the South Motagua Suture Zone: One where eclogitization initiates at 300 °C and 1.1 GPa and continues to 480 °C and 2.6 GPa (Tsujimori et al., 2006b), and another where eclogitization initiates at 470 °C and 2 GPa and continues to 520 °C and 2.5 GPa (Endo et al., 2012). In order to resolve which of these two P-T paths is more likely to be correct and to provide better constraints on the prograde P-T-t path, I combine petrographic analyses, elemental zoning in garnet (both

major and trace), and Sm-Nd garnet-whole rock geochronology to get a better picture of the processes going on during the prograde path of this subduction zone.

4.2: GEOLOGICAL SETTING

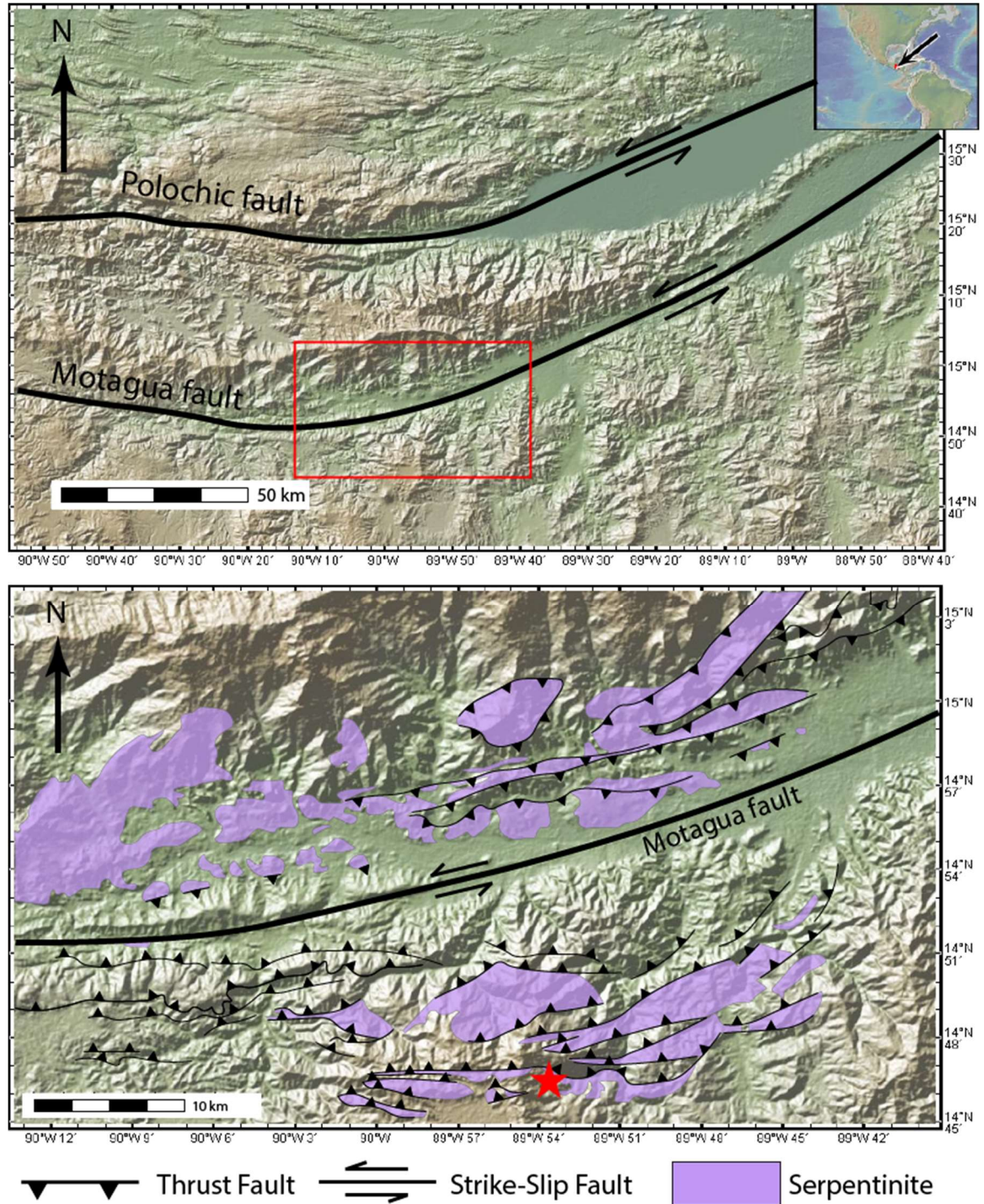


Figure 4.1: The Motagua fault is a left-lateral strike-slip fault located in central Guatemala. This map was modified from an original, unpublished map by Sisson (personal communication 2014).

The Motagua Suture Zone in central Guatemala is bound to the north and south by the exhumed remains of two separate subduction zones (Figure 4.1) that have been juxtaposed across the fault by more than 1100 km of displacement since the Eocene (Rosencrantz and Mann, 1991). Until recently, it was thought that these two serpentinite mélange belts were the remnants of one collisional event that occurred in the Late Cretaceous. Recent research in this area has resulted in the determination that these two mélange belts experienced very different exhumation histories, but perhaps similar subduction histories (e.g., Harlow et al., 2004; Brueckner et al., 2009).

These serpentinite mélange belts serve as host to HP metamorphic assemblages, with the mélange to the north containing zoisite eclogite and the mélange to the south containing lawsonite eclogite. These two eclogites formed under very different conditions, with the northern eclogite experiencing peak P-T conditions of 620 °C and 1.7 GPa and the southern eclogite experiencing prograde P-T conditions of 300-480 °C and 2-2.5 GPa (Tsujimori et al., 2004; Tsujimori et al., 2006b; Bonnet et al., 2014).

Additional differences between the north and the south include the age of metamorphism. Sm-Nd dates from both sides of the fault reveal similar prograde ages ranging from 140-120 Ma (Brueckner et al., 2009). In contrast, $^{40}\text{Ar}/^{39}\text{Ar}$ ages from both sides of the fault are quite different, with exhumation ages of 77-65 Ma north of the fault, and 125-113 Ma south of the fault (Harlow et al., 2004).

Final exhumation of these assemblages is relatively recent, with fission track and Zircon (U-Th)/He thermochronology placing the uplift of the mountains to the south of the fault at 24-16 Ma and the mountains to the north of the fault at 55-31 Ma (Francis,

2005; Simon-Labrie et al., 2013). This uplift was caused by transpression along the Motagua fault, which continues today (Rogers et al., 2002). The juxtaposition of these two mélangé belts can thus be explained by a more recent exhumation, rather than exposure and then a 1100 km displacement along the Motagua fault (Brueckner et al., 2009).

4.3: METHODS

4.3.1: Major Element Concentration

Electron probe microanalyses (EPMA) of garnet were conducted using a Cameca SX50 electron microprobe at the University of Houston. Central profiles of garnet and sample selection were determined through a combination of geometric and compositional analysis. Geometric analysis involved determining the core location of garnet through measuring the maximum diameter across garnet grains and determining the central point and collecting major element profiles starting at the rim of garnet and proceeding to the mapped core of the garnet. Compositional analysis involved six spot analyses per garnet, three for core concentration and three for rim concentration and comparing Mn compositions, selecting samples that have the highest Mn concentration at the core to increase likelihood of garnet samples representing true central cuts. Quantitative analyses of major element concentrations were conducted with 15 kV accelerating voltage at 20 nA beam current, with a 10 µm spot size. Standard calibration was conducted using the University of Houston garnet standard. Profiles were created by spot analyses every 15 µm, skipping over detectable mineral inclusions and fractures. Conversion of weight % oxide into mole fraction was completed using MINERAL (De Angelis and Neill, 2012).

4.3.2: Trace and REE Concentration

In situ trace element analyses were performed using a Photon Machines Analyte.193 laser ablation instrument coupled to a Varian 810-MS quadrupole ICP-MS at the University of Houston. Prior to analysis, major element composition was measured by EPMA at the University of Houston. Trace element and REE analysis includes: ^7Li , ^{11}B , ^{25}Mg , ^{29}Si , ^{29}Sc , ^{51}V , ^{52}Cr , ^{55}Mn , ^{59}Co , ^{88}Sr , ^{89}Y , ^{91}Zr , ^{93}Nb , ^{95}Mo , ^{137}Ba , ^{139}La , ^{140}Ce , ^{141}Pr , ^{146}Nd , ^{149}Sm , ^{151}Eu , ^{157}Gd , ^{159}Tb , ^{163}Dy , ^{165}Ho , ^{166}Er , ^{169}Tm , ^{173}Yb , ^{175}Lu , and ^{178}Hf . Garnet was analyzed with a spot size of 50 μm and lawsonite and phengite with a spot size of 15 μm . Each analysis was preceded by a gas blank of ~ 18 s. Samples were then ablated for ~ 25 s with a laser power of 3 mJ at a 4 ns pulse with a repetition rate of 10 Hz for garnet and 12 Hz for lawsonite. All trace element data was corrected for laser and ICP-MS element fractionation with internal elements Mg for garnet and Si for lawsonite calibrated by EPMA and USGS external standard BHVO-2G glass using the commercial data reduction software Glitter.

4.3.3: X-ray Element Maps

X-ray element maps were collected on the Cameca SX 100 at the American Museum of Natural History. Analysis conditions for the microprobe are a beam current of 80 nA, and accelerating voltage of 15 Kv, a dwell time of 85 ms, a beam diameter of 1 μm , and a step size of 3 μm . Elemental maps were produced for Si, Ti, Al, Mg, Fe, Mn, Ca, K, Na, and Ba. These element maps were processed using XMapTools version 2.5.2 (Lanari et al., 2014; Lanari et al., 2018) in order to create weight percent oxide maps.

4.3.4: Sample Preparation for Sm-Nd Isotopic Analysis

Eclogite sample MVE12-66-1 was prepared for analysis through first crushing the sample with a combination of sledge hammer and then steel mortar and pestle. Crushed samples were then put through a series of metal sieves and separated into several grain size populations. Grain size population $\sim 150\text{ }\mu\text{m}$ - $\sim 250\text{ }\mu\text{m}$ was chosen for analysis due to the population striking a balance between inclusion-free garnet population and a grain size that could be separated manually. Garnet was hand-picked for inclusion-free grains, which biased this population to the inclusion-free rim of the garnets, which would naturally bias the Sm-Nd age to a younger age. Further populations that were separated included: clinopyroxene, bulk rock, and lawsonite.

4.3.5: Leaching for Sm-Nd Isotopic Analysis

Picked garnet was then leached to remove any possible inclusions that may have been too small to see using a microscope. Leaching began with 2 mL of 6 mol HCl + 0.2 mol HF for 30 min at 80 °C on a hot plate, after which the leachate was removed and placed into another Teflon beaker. The garnet was then rinsed twice with 1.5 mL of mill-Q H₂O and this was also placed in the leachate beaker, and the sample was left to dry down overnight at 75 °C. The next round of leaching involved the addition of 2 mL of 6 mol HCl + 0.2 mol HF and sitting in the Ultra Sonik at 55 °C for 30 min, rinsed twice with 1.5 mL of mill-Q H₂O, with the leachate being set aside in its beaker. This process was repeated once more at the same conditions. An additional leaching in the Ultra Sonik was done with 2 mL of 6 mol HCl for 2 h, then rinsed twice with 1.5 mL of mill-Q H₂O, with the leachate being set aside for analysis. Garnet was then dried and split in half, with

garnet population A being leached one additional time in 1 mL of 6 mol HCl at 80 °C overnight.

4.3.6: Digestion and Analysis

Sample digestion began with 4 mL 29 M HF + 0.5 mL 15 M HNO₃, which was then allowed to dry down. The next run involved 2 mL 29 M HF + 300 µL 15 M HNO₃, once again dried down. The following digestion run consisted of 2 mL 15 M HNO₃ + 1 mL 29 M HF + 1 mL HCL, then dried down. This run was followed then by another with 2 mL 15 M HNO₃ + 2 mL mill-Q H₂O and heated overnight at 110 °C. After drying down the next day, 4 mL 8 M HNO₃ was added and allowed to sit over a weekend. Following this, there were four rounds of adding 4 mL of 6 M HCl that would heat overnight at 110-120 °C, drying down the next day before starting over again.

After sample digestion, the UH concentrated Sm-Nd spike was added to the samples. From this point, REE separation was accomplished using cation exchange resin and 6 M HCl. Afterwards, Sm and Nd were further separated using exchange resin and methyllactic acid. After separation, samples were loaded into the Nu Instruments Plasma II – MC-ICP-MS for analysis.

4.4: PETROGRAPHY

4.4.1: MVE12-66-1

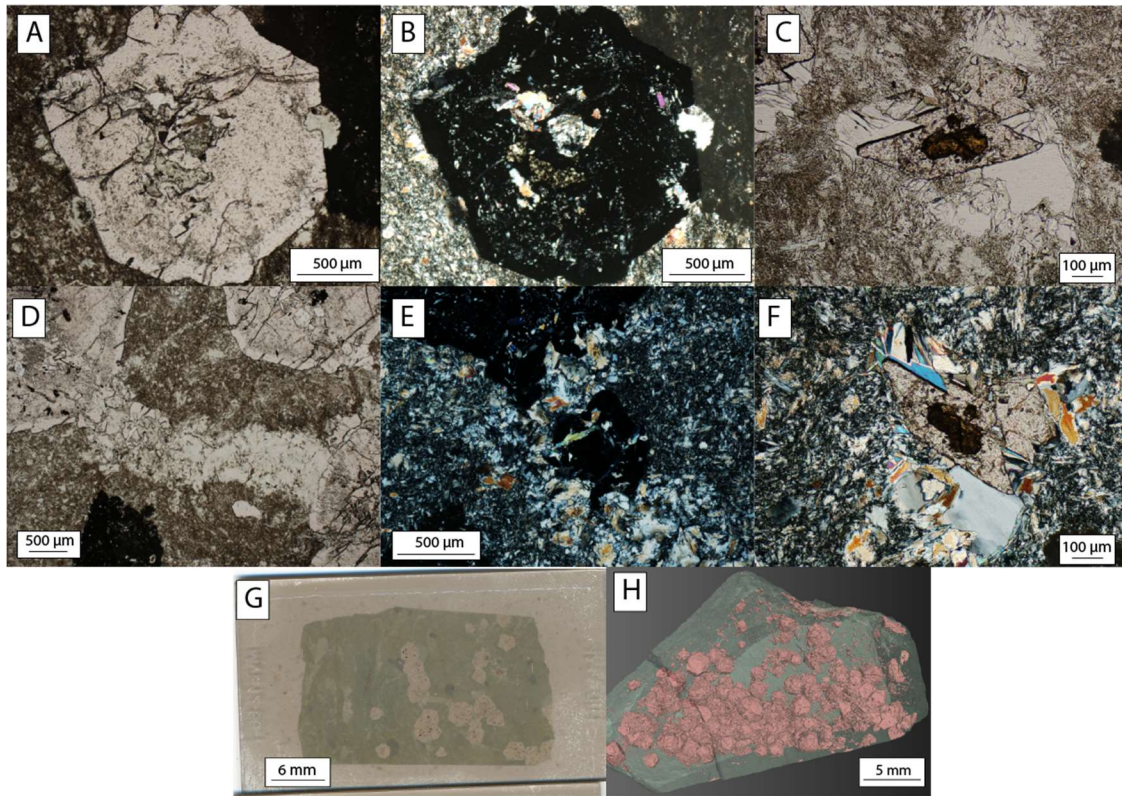


Figure 4.2: Thin section images of MVE12-66-1. A) Plane polarized light of sample 4, subidioblastic grain shows a continuous inclusion-poor rim surrounding the garnet. B) Cross-polarized light image of sample 4, abundance of large inclusions in the core of the garnet gives way to smaller inclusions away from the core. C) Plane polarized light of idioblastic titanite overgrowth surrounding rutile. D) Lawsonite vein with intragranular quartz and small garnet. E) Higher magnification, plane polarized light image of lawsonite vein highlighting small garnet in center of image. F) Plane polarized light of titanite overgrowth. G) Thin section image of MVE12-66-1, showing planar distribution of intergrown garnet. H) 3D model of eclogite sample constructed using CT data. Garnet appears dominantly as clusters.

Eclogite sample MVE12-66-1 is characterized by a granoblastic matrix of omphacite, garnet, lawsonite, phengite, titanite, rutile, and some quartz. Matrix foliations are difficult to identify, although garnet appears to grow preferentially in planar masses (Figure 4.2 G), with near-oriented lawsonite as inclusions. Garnet (1-4 mm) contains

inclusion-rich cores with inclusions of ilmenite, chlorite, euhedral lawsonite, phengite, and minor rutile (Figure 4.2 A and B). Garnet grains have inclusion-free rims. Chlorite and lawsonite occur as inclusions only in the core of garnets. Late-stage phengite occurs along garnet grain boundaries and occasionally fills cracks in garnet grains. Veins of lawsonite and some omphacite and intergrown quartz connect subidioblastic grains of garnet, with garnet growing into the veins outward from original grain boundaries (Figure 4.2 D and E). Titanite occurs in two forms in this sample: as poikiloblastic, xenoblastic porphyroblasts, or as idioblastic, prismatic overgrowths around rutile (Figure 4.2 C and F).

4.4.2: MVE12-66-4

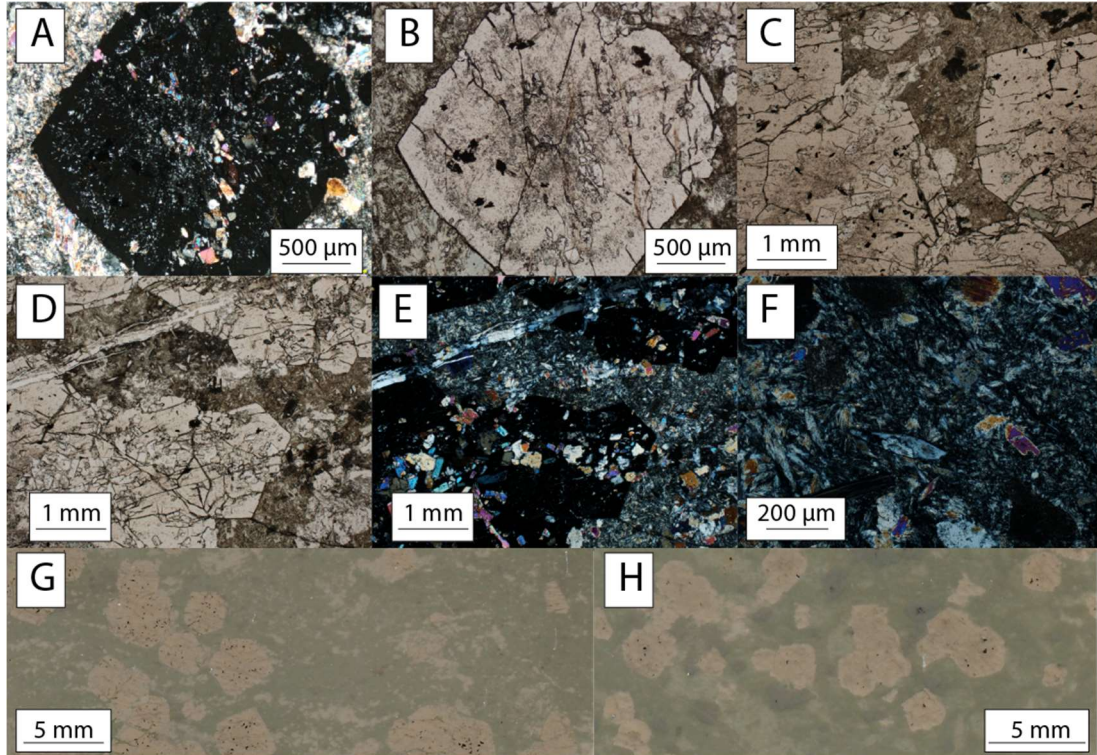


Figure 4.3: Thin section images for MVE12-66-4. A) Cross-polarized light image of idioblastic garnet sample with an abundance of inclusions and an inclusion-poor rim. B) Oriented inclusions could preserve S_1 foliation. C) Lawsonite inclusions in garnet are commonly idioblastic. Fractures in garnet are commonly filled with chlorite, which is discontinuous with the matrix. D) Large inclusions follow discrete bands in garnet. E) Fractures in eclogite are commonly filled with quartz, albite, and calcite. F) Lens-shaped quartz. G) Thin section image of MVE12-66-4-002. H) Thin section image of MVE12-66-4-003.

Eclogite sample MVE12-66-4 is characterized by a granoblastic matrix of omphacite, garnet, titanite, quartz, and lawsonite. A weak S_1 foliation is preserved by oriented inclusions in garnet (Figure 4.3 A and B). Garnet (1-4 mm) contains inclusions of idioblastic lawsonite, ilmenite, and chlorite. Garnet grains are subidioblastic and dominantly occur as intergrown crystals rather than as distinct grains, though some independent grains do occur (Figure 4.3 C). Titanite occurs in polycrystalline masses, and

is xenoblastic. Little rutile remains, and it is likely that all rutile has been transformed into titanite during retrograde processes. Quartz in the matrix occurs as lens-shaped grains (Figure 4.3 F). Fractures are parallel and continuous through garnet and are filled with quartz, albite, and calcite (Figure 4.3 D and E). These filled fractures are also oriented parallel to fractures present in all garnet porphyroblasts.

4.4.3: MVE12-66-5

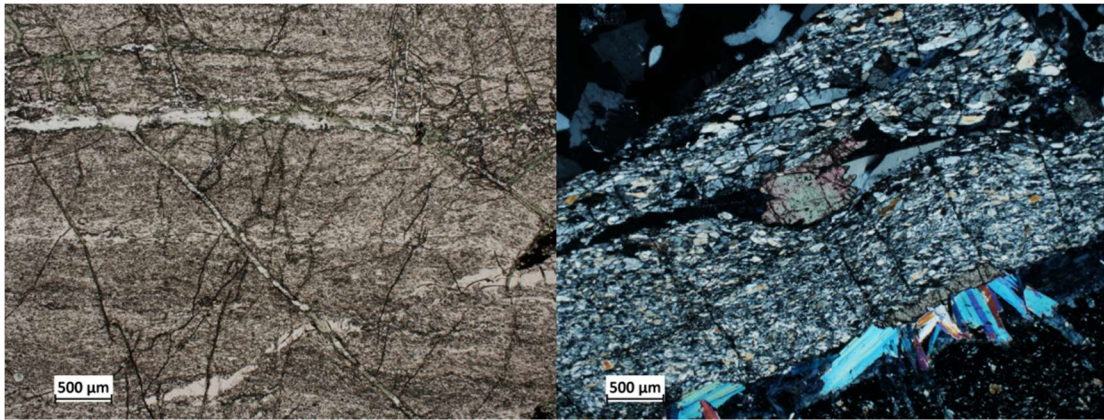


Figure 4.4: Garnet grains are massive and subidioblastic with defined inclusion trails that are continuous with foliation in the matrix (Left). Titanite appears to preserve pressure shadows (Right).

Eclogite MVE12-66-5 is composed of omphacite, large (1-4 cm) garnet porphyroblasts, minor lawsonite, phengite, and chlorite (Figure 4.4). Matrix is nematoblastic with S_1 foliation preserved by prismatic omphacite and oriented titanite. S_1 foliation appears to be mostly continuous with inclusion trails in garnet, though much of it is obscured by fractures. Garnet contains inclusions of rutile, titanite, omphacite, and lawsonite and is subhedral. Much of the original garnet has been severely retrogressed, with abundant fractures filled with chlorite and phengite. In some locations, upwards of 50% of the original garnet has been retrogressed to chlorite. Fractures that intersect with

rutile inclusions show rutile replaced by titanite. Original garnet rims have been destroyed during retrograde processes that have retrogressed garnet to chlorite. Garnet also contains fractures parallel to the internal foliation that have been filled in with a mixture of phengite, chlorite, and quartz.

4.4.4: MVE12-66-7

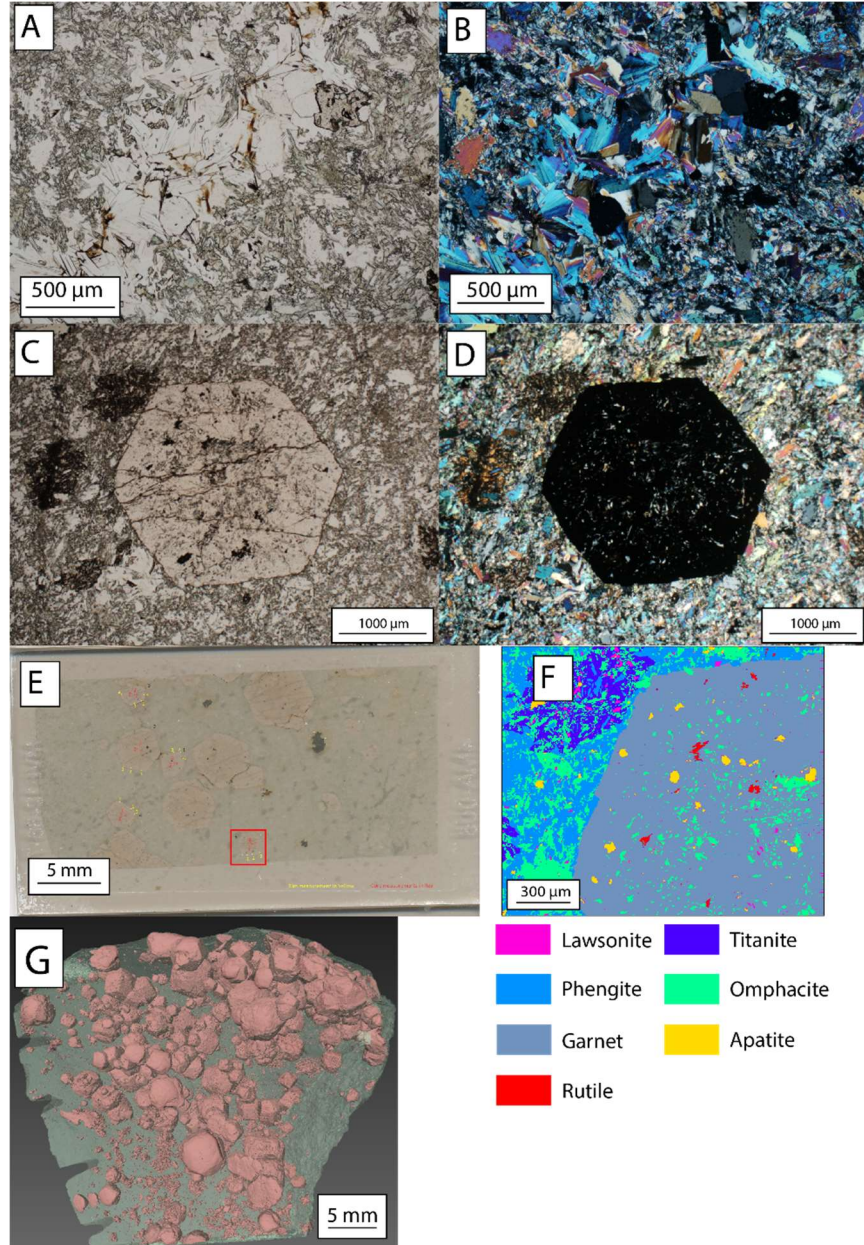


Figure 4.5: Thin section images and mineral map for MVE12-66-7. A) Vein containing lawsonite, phengite, titanite, quartz, and garnet. B) Cross-polarized light image of vein highlighting inclusion-poor nature of garnet. C) Garnet is largely idioblastic and contains abundant inclusions. D) The inclusion-poor rim is still visible, but not as distinct. E) Thin section image shows wider distribution of garnet and pyrite. F) Mineral map shows wide variance in the amount of inclusions present, as well as the small size of inclusions. G) Projection of a 3D image of eclogite sample created from CT data.

Eclogite MVE12-66-7 is composed of omphacite, euhedral garnet (2-10 mm), abundant phengite, poikiloblastic titanite, and pyrite. Garnet is commonly intergrown, but with an abundance of independent grains as well. Garnet contains inclusions of omphacite, ilmenite, apatite, and minor chlorite and clinozoisite (Figure 4.5 C, D and F). Chlorite also occurs as fill in fractures in garnet. Garnet has common iron oxide staining along fractures and some grain boundaries. Garnet has inclusion-poor rims without the same marked boundary observed in MVE12-66-1. The transition to inclusion-poor rim begins ~300 μm from the rim and is characterized by a decrease in mineral inclusions. Lawsonite occurs dominantly in veins or as inclusions in poikiloblastic titanite and rarely as inclusions in garnet. Lawsonite in garnet is smaller than 1 μm . Veins occurring in this sample are filled with a mixture of large phengite, lawsonite, titanite, quartz, recrystallized omphacite, and small garnets (Figure 4.5 A and B). Staining suggest a possible hydrous source, possibly from same event that resulted in the formation of pyrite.

4.4.5: MVE12-67-1

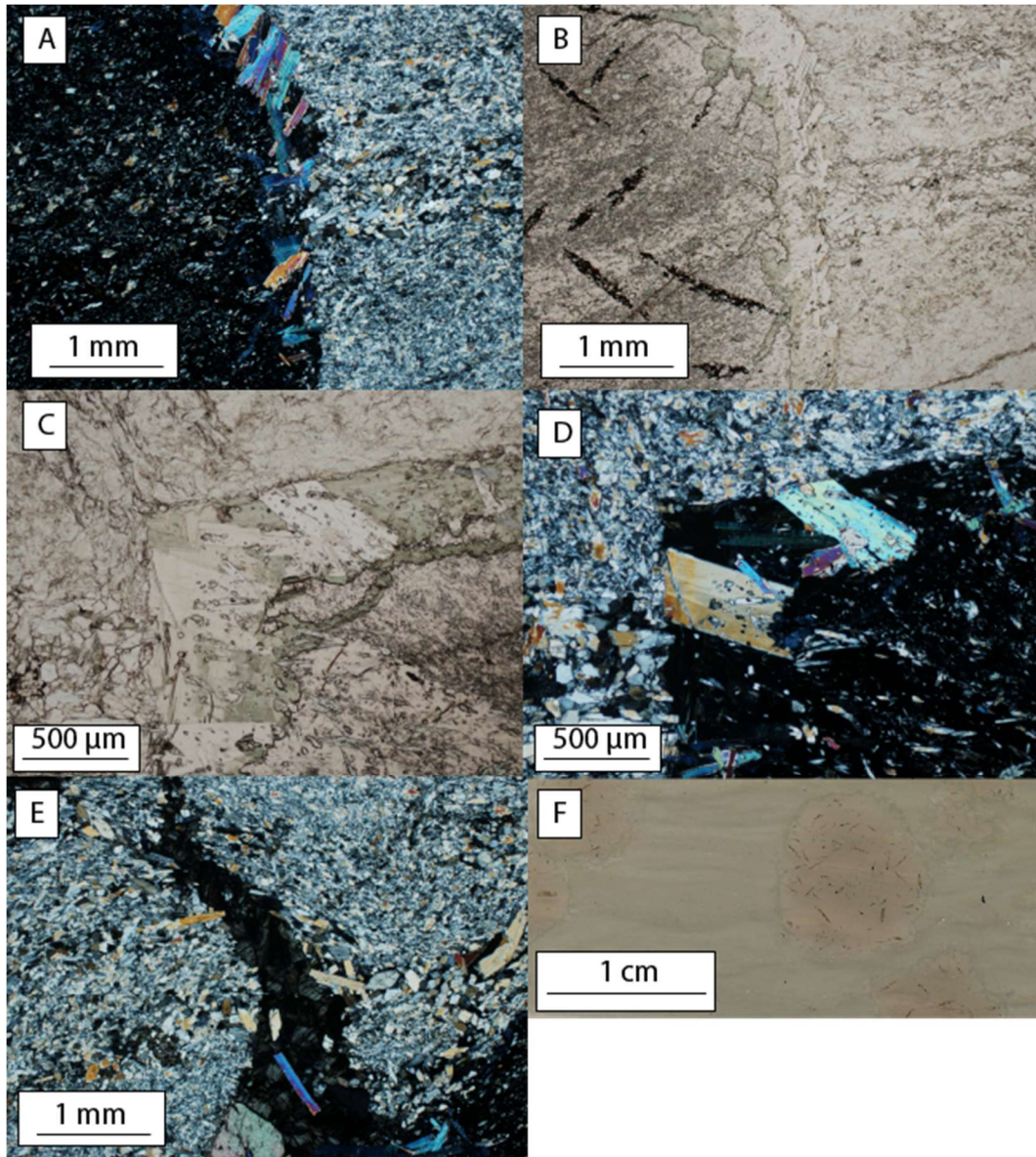


Figure 4.6: Thin section images of MVE12-67-1. A) Cross-polarized light image of garnet shows abundance of mineral inclusions. B) Foliation preserved by mineral inclusions in garnet is parallel with foliation in the matrix and dark rutile. C) Reaction rim around garnet appears to preserve original grain boundary of garnet, with chlorite filling fractures. D) Reaction rim around garnet is substantially coarser than matrix. E) Chlorite veins are present in the matrix. F) Thin section scan of MVE12-67-1 shows S_1 foliation preserved by inclusion trails in garnet with S_2 parallel to sub-parallel in the matrix.

Eclogite MVE12-67-1 is foliated with coarse-grained omphacite and lawsonite defining the S_2 foliation and inclusion trails in garnet preserving the S_1 foliation (Figure 4.6). The sample is composed of omphacite, xenoblastic garnet (0.5-1.5 cm), chlorite, phengite, titanite, and minor lawsonite. Garnet contains inclusions of chlorite, omphacite, minor glaucophane, phengite, and small lawsonite, and large rutile inclusions. Inclusion trails in garnet are parallel. Garnet has reaction rims completely surrounding garnet grains. These rims are composed of chlorite, phengite, minor glaucophane, titanite, and prismatic omphacite with compositionally zoned larger sodic pyroxene, and minor lawsonite. Veins are composed of chlorite, phengite, and titanite, with prismatic omphacite. These veins are oriented randomly, cutting across and sometimes parallel to foliation.

4.4.6: MVE12-68-3

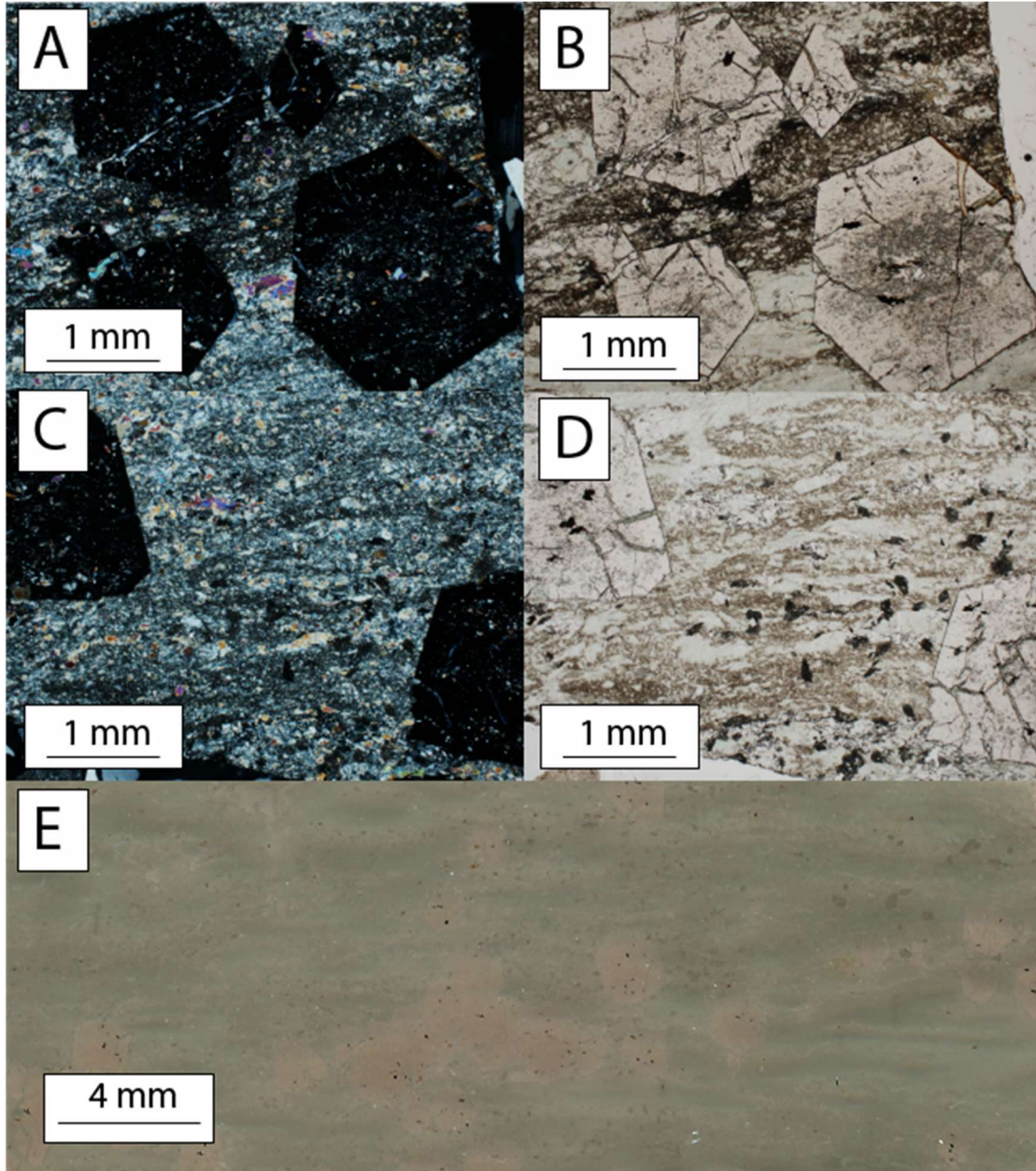


Figure 4.7: Thin section images of MVE12-68-3. A and B) Garnet in this sample has abundant inclusions that decrease in frequency closer to the rim. C and D) Foliation is well preserved in the matrix by coarse grained omphacite and lawsonite. E) Thin section highlights foliation present in the matrix.

Eclogite sample MVE12-68-3 contains a granoblastic matrix with an S_1 foliation preserved by omphacite and lawsonite (Figure 4.7). This sample contains omphacite, garnet (1-4 mm), titanite, lawsonite, and phengite. Garnet inclusions include lawsonite (small, euhedral), ilmenite, apatite, rutile, omphacite, and chlorite abundant in the core. Garnet contains relatively inclusion-poor rims that begin $\sim 300\ \mu\text{m}$ from the rim. Ilmenite is present throughout as well. Fracture-fill in garnet is chlorite and is not continuous with the matrix. This happens most often at grain boundaries between nearly-intergrown garnet grains. Both lawsonite and omphacite in the matrix occur as either prismatic grains or as granoblastic masses. Retrograde titanite is present throughout the matrix. Lawsonite can be found as both inclusions in garnet and in the matrix.

4.5: RESULTS

4.5.1: Major Element

Major element concentration profiles were collected for three lawsonite eclogite samples: MVE12-66-1, MVE12-66-4, and MVE12-66-7. These samples were selected due to the pristine nature of the garnet that have not been obscured by retrograde processes, which were observed for MVE12-66-5, MVE12-67-1. Major element profiles measured for MVE12-66-1 (Figure 4.8) and MVE12-66-4 (Figures 4.9, 4.10 and 4.11) are similar and have been analyzed in detail in Chapter 2 and will be described together, with MVE12-66-7 being described separately.

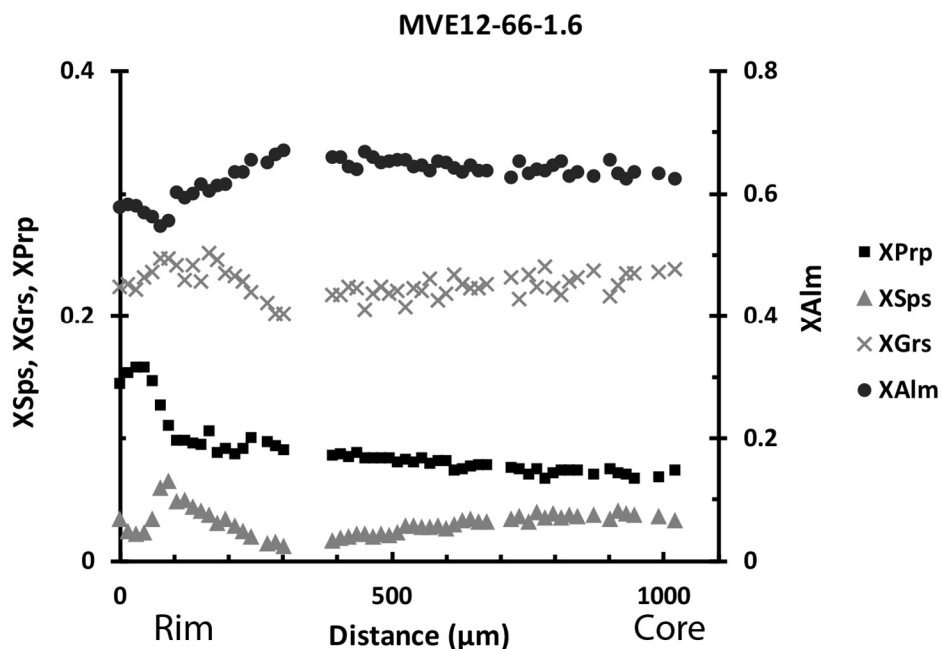


Figure 4.8: Garnet end member zoning profile for MVE12-66-1.6. Gaps in concentration profile are the result of omission due to presence of inclusions. Zoning profile for this sample is virtually identical to that of MVE12-66-1.5, regardless of size.

Almandine core compositions between these samples is very similar, consisting of 0.62-0.67 XAlm. Moving outward from the core, MVE12-66-1.6 (Figure 4.8) shows an increase in XAlm from 0.62 to 0.67, with this increase ceasing at ~300 μm from the rim. For MVE12-66-4, XAlm composition is consistent from the core to 200-300 μm from the rim, dependent on grain size, with the smaller the grain radius the closer to the rim this constant composition ends. At these respective points in garnet, the almandine component in each sample begins to decrease. In MVE12-66-1, XAlm decreases from 0.67 to a minimum of 0.55 before increasing to a constant composition of 0.56. Garnet from MVE12-66-4 has similar XAlm zoning in this region, with a decrease from 0.66 to 0.54 before reaching constant composition of 0.57 XAlm in the rim. MVE12-66-4-003.7

is anomalous in that it lacks a constant composition at the rim, instead decreasing in almandine component from 0.66-0.54.

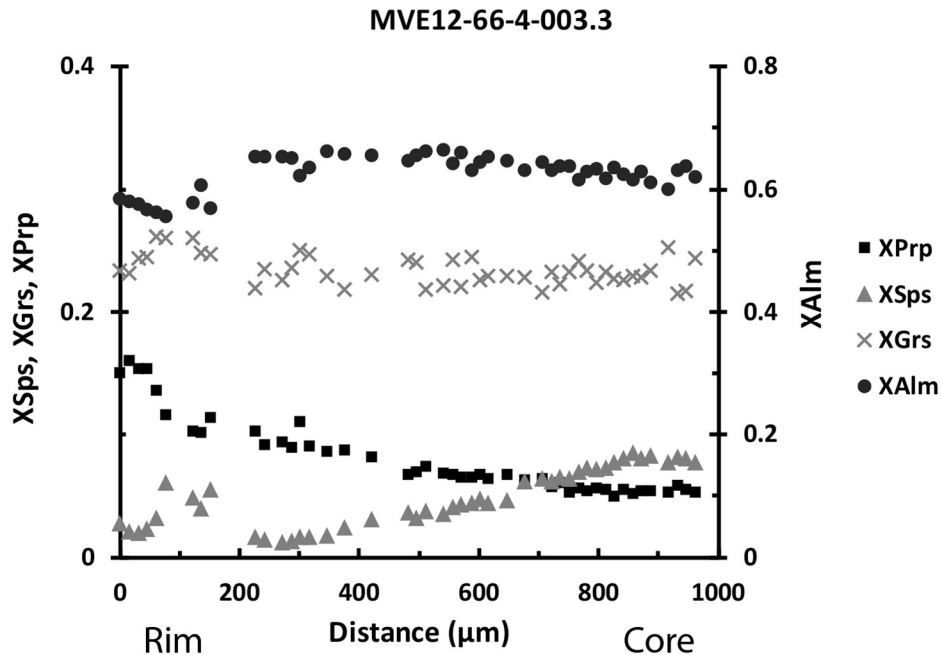


Figure 4.9: Garnet end member zoning for MVE12-66-4-003.3. Ca zoning is less well defined in this sample. This may be the result of patchy zoning that has been observed in the x-ray element map for MVE12-66-7.5.

The grossular zoning is irregular in most garnet samples with only general trends visible. MVE12-66-1.6 (Figure 4.8) has a core composition of 0.24 XGrS, which decreases steadily to 0.2 at 300 μm from the rim, then increases to 0.25 XGrS at 90 μm from the rim, where it then decreases to 0.22 at the rim. For MVE12-66-4, most garnet follows a similar pattern, with an average core XGrS composition of 0.23, with irregular concentrations throughout the garnet core varying between 0.21-0.24. This remains consistent until $\sim 300 \mu\text{m}$ for most samples, where an increase in XGrS from 0.21 to 0.26 at $\sim 200 \mu\text{m}$ from the rim is easiest to see in MVE12-66-4-003.9 (Figure 4.11) but has been obscured in MVE12-66-4-003.3 (Figure 4.9) due to a gap in the data caused by

skipping an inclusion. After this point, grossular content decreases to a similar concentration as the core. Once again, MVE12-66-4-003.7 (Figure 4.10) follows a similar core composition and zoning, with an increase in XGrs of 0.21 to 0.24 from 200 μm from the rim to the rim.

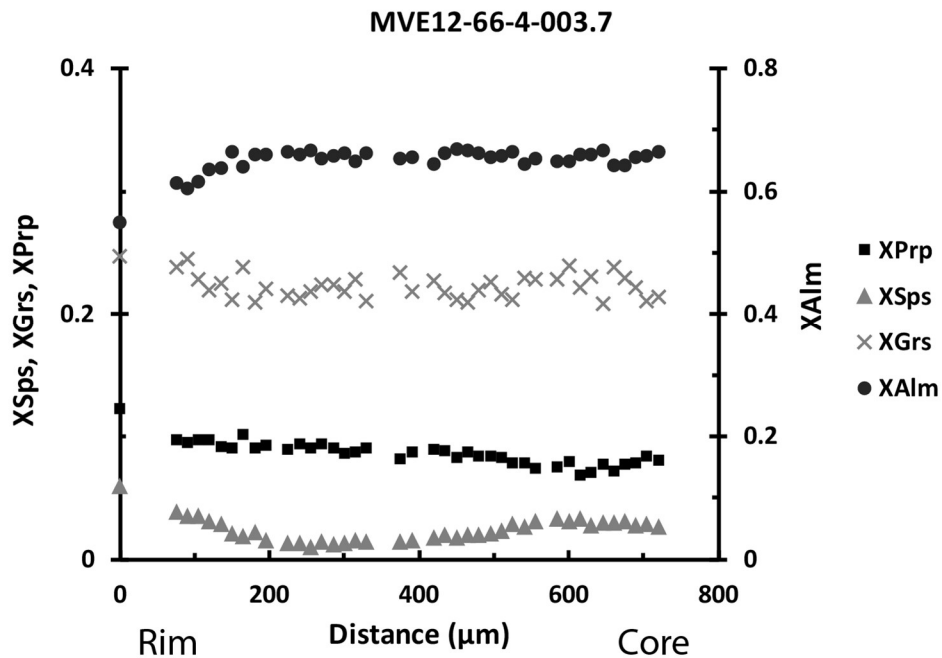


Figure 4.10: Garnet end member profile for MVE12-66-4-003.7. This end member profile is missing the secondary growth zone that has been identified in other garnet samples from MVE12-66-1 and MVE12-66-4.

Pyrope content increases across all garnet samples for MVE12-66-1 and MVE12-66-4. Pyrope content in MVE12-66-1 increases gradually from 0.07 at the core to 0.09 100 μm from the rim, where it increases sharply to 0.16 at 30 μm from the rim, before decreasing slightly to 0.15 at the rim. In MVE12-66-4, core compositions of pyrope increase gradually from an average minimum of ~ 0.07 to an average of 0.09 at ~ 100 μm from the rim for most samples except MVE12-66-4-003.7 (Figure 4.10), which ends with this gradual increase in pyrope content. Other samples from this eclogite continue to

increase sharply to an average of ~ 0.16 . From this point, these samples see a gradual decrease in pyrope content to 0.15 at the rim.

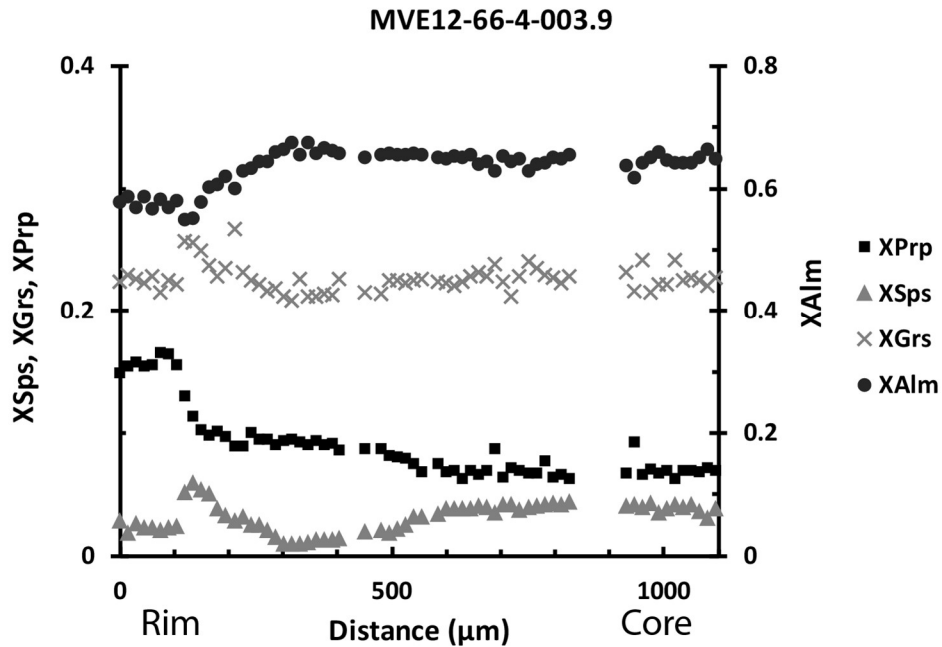


Figure 4.11: Garnet end member zoning for garnet sample MVE12-66-4-003.9. Garnet end member zoning for this sample is among the best defined of those taken from eclogite sample MVE12-66-4. Rim increase of Mn remains consistent with other samples but displays a well-defined plateau-like composition in the 100 μm at the rim. Other major elements follow along with this concentration zoning, with a well-defined concentration at the rim.

Spessartine content is sensitive to changes in pressure and temperature and often records discrete changes in these conditions at the micron scale (Banno and Chii, 1978; Săbău et al., 2006). As expected for prograde zoned garnet, all spessartine content follows a bell-shaped curve from the core to partway towards the rim (Hollister et al., 1966; Lapen et al., 2003; Skora et al., 2006). This bell-shaped curve ends $\sim 300 \mu\text{m}$ from the rim for each garnet sample in MVE12-66-1 and MVE12-66-4. At this point, Mn increases from ~ 0.01 to ~ 0.07 XSps over a variable distance ending between 75-120 μm

from the rim in most samples. The one exception is MVE12-66-4-003.7 (Figure 4.10), which ends with an increase in Mn at the rim. The other samples see a sharp decrease of Mn at this point from ~ 0.07 to ~ 0.03 over the span of $\sim 40 \mu\text{m}$.

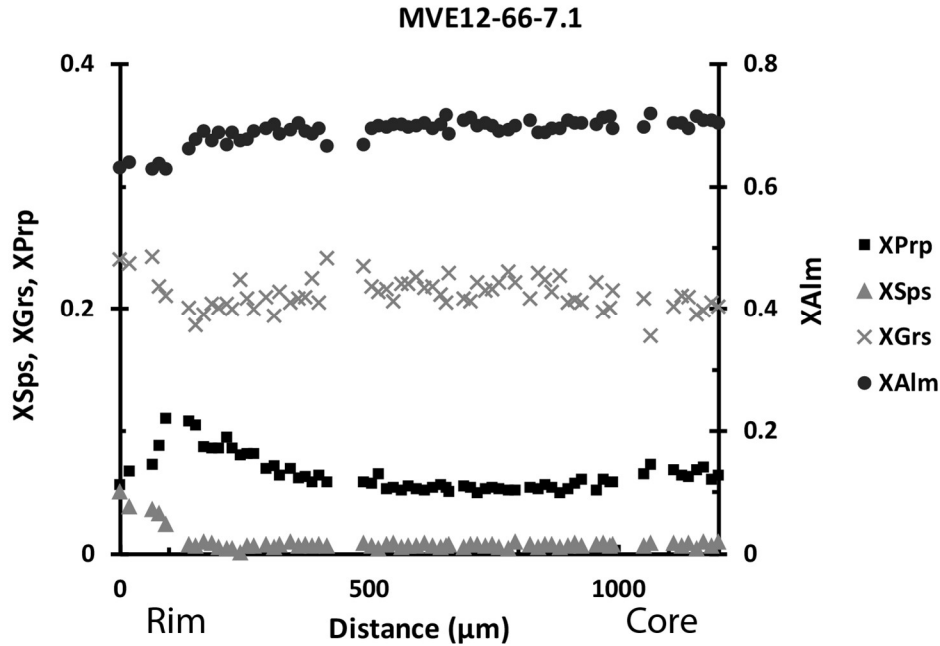


Figure 4.12: Garnet end member zoning profile for MVE12-66-7.1. Garnet end member zoning for all garnets in MVE12-66-7 follows slightly different chemical zoning than those shown in other eclogite samples. Mn is missing its large inner peak concentration in most samples. This is the only sample that preserves a major decrease in its almandine component in the rim.

Major element zoning for garnet in MVE12-66-7 is markedly different than those measured for other eclogite samples. The most obvious of these at first glance is zoning in spessartine content. Typically, one expects to see bell-curve zoning for garnet (Hollister et al., 1966; Lapen et al., 2003; Skora et al., 2006), but this bell-shaped curve is missing in all samples except a subtle one in MVE12-66-7.5 (Figure 4.15). In this sample, core compositions average around 0.013 and steadily decrease to ~ 0.006 at 975 μm from the rim, where compositions oscillate from 0.006 to 0.008 until $\sim 200 \mu\text{m}$ from

the rim, where spessartine content increases from 0.004 to 0.06 XSps at the rim. Though most other samples are missing the central peak in spessartine content, they all share an oscillatory zoning in in this component, which is particularly pronounced at the rim, where XSps increases in all samples.

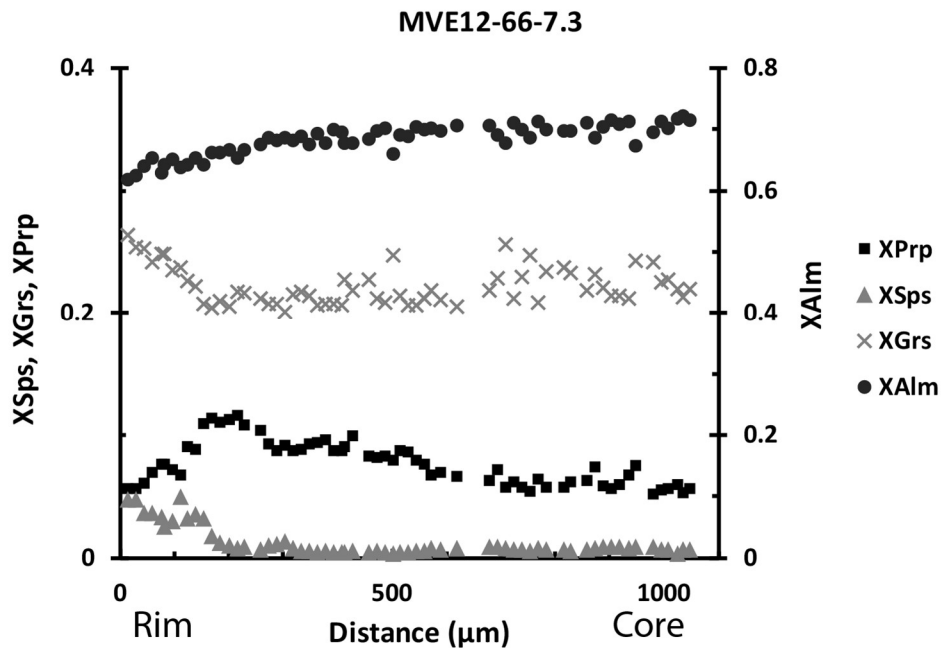


Figure 4.13: Garnet end member profile for MVE12-66-7.3. Inclusions in the garnet sample serve to obscure grossular component but have little effect on other end member concentrations. Spessartine component preserves oscillatory zoning that has been frequently observed in garnet from this region (Tsujimori et al., 2006b; Tsujimori et al., 2012; Bradley et al., in preparation). Pyrope component also appears to preserve oscillatory zoning between 200-600 μm from the rim. Major disruption in chemical zoning begins 200 μm from the rim.

Almandine content is also different between the measured profiles for prior eclogite samples and this sample. The sample with the most in common with prior samples is MVE12-66-7.1 (Figure 4.12). This sample has a plateau-like composition of XAlm across most of the garnet that averages 0.7 until 138 μm from the rim, where XAlm decreases to 0.63 and remains roughly at that composition until the rim. Other

garnet samples have a similar plateau-like concentration profile across most of the garnet with an average composition that varies between ~ 0.68 - 0.7 . For these samples, there is a gradual decrease in X_{Alm} that begins at variable distances from the rim. MVE12-66-7.3 (Figure 4.13) has the most gradual decrease of X_{Alm} , which begins at approximately $270\ \mu\text{m}$ from the rim, with almandine content decreasing from ~ 0.68 to 0.62 at the rim. For MVE12-66-7.4 (Figure 4.14), X_{Alm} begins to decrease at $\sim 120\ \mu\text{m}$ from the rim, with X_{Alm} decreasing from 0.68 to 0.65 . MVE12-66-7.5 (Figure 4.15) also follows this zoning, with a decrease in concentration beginning around $135\ \mu\text{m}$ from the rim and results in a decrease from 0.69 to 0.59 at the rim.

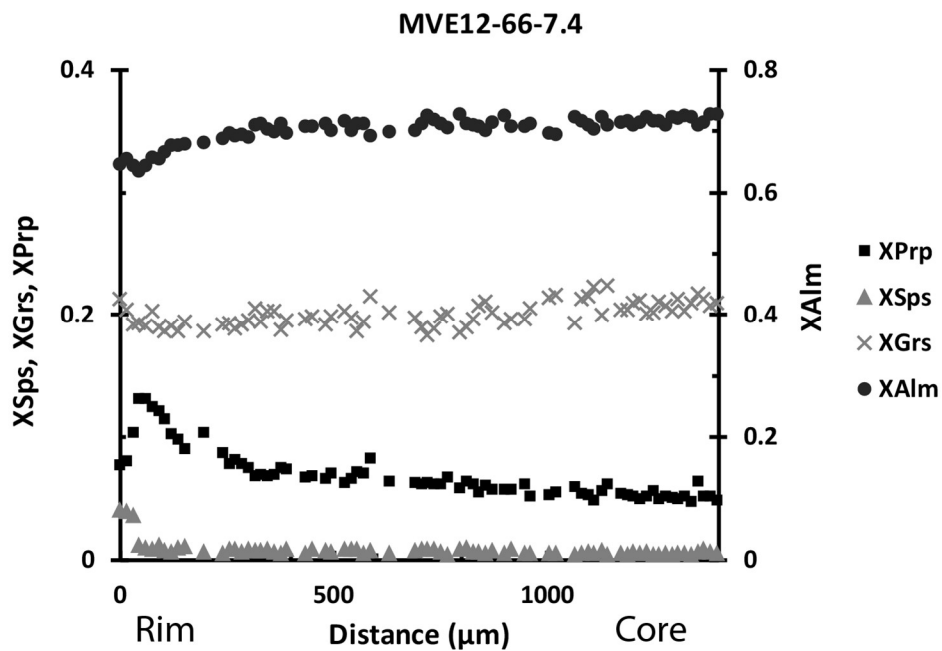


Figure 4.14: Garnet end member zoning for MVE12-66-7.4. The rim zoning that has been observed in other samples is nearly completely missing in this sample, with only a small band $\sim 50\ \mu\text{m}$ from the rim preserving the decrease in Mg and increase in Mn that has been observed in other samples.

Grossular content in these samples follows a trend that generally follows that of Mn respective to each sample. Core compositions in many of the garnet samples are highly variable (Figure 4.12, 4.13, and 4.15). This irregular core composition can be seen in the X-ray element map for MVE12-66-7.5 (Figure 4.16) as splotchy regions of higher CaO concentrations across the garnet. This zoning that follows the same trend as that of XSps is most evident in an increase in XGrs at the rim that begins at the same point as XSps increase for each garnet sample.

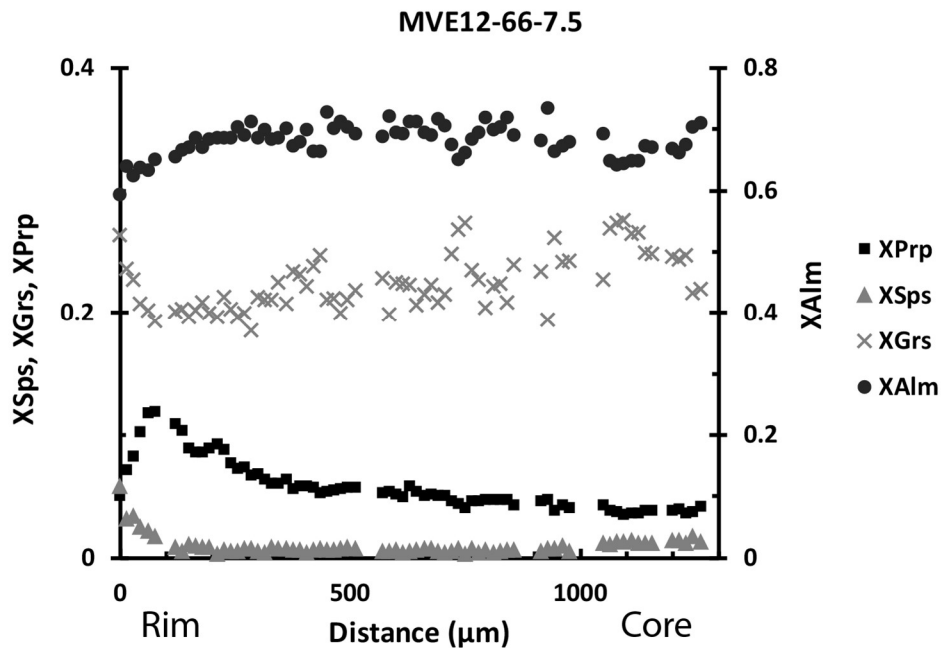


Figure 4.15: Garnet end member zoning for MVE12-66-7.5. This sample preserves the highest concentration for Mn at the core between measured garnet for this eclogite sample. CaO zoning for this sample is nearly obscured, which would indicate variance introduced by inclusions.

Pyrope content for garnet in MVE12-66-7 follows similar trends, with the greatest variance at the increased concentration rim band. MVE12-66-7.4 (Figure 4.14) and MVE12-66-7.5 (Figure 4.15) are near-identical in XPrp zoning, with a gradual increase

from the core to $\sim 300 \mu\text{m}$ from the rim, where both samples have an oscillatory zoning, increasing XPrp in the samples by ~ 0.06 over a span of 200-270 μm , before decreasing by ~ 0.07 at the rim. MVE12-66-7.1 (Figure 4.12) has a slight increase of XPrp at the core of garnet, with average composition of 0.06, that decreases slightly from the core to ~ 0.05 midway from core to rim. From $\sim 500 \mu\text{m}$ from the rim to $\sim 138 \mu\text{m}$ from the rim, XPrp begins to increase gradually from ~ 0.05 to 0.11. At $\sim 92 \mu\text{m}$ from the rim, XPrp begins to decrease from 0.11 to 0.06 at the rim. Pyrope content in MVE12-66-7.3 (Figure 4.13) increases from 0.06 at the core to 0.12 at 215 μm from the rim. After this point, pyrope content decreases to 0.06 at the rim.

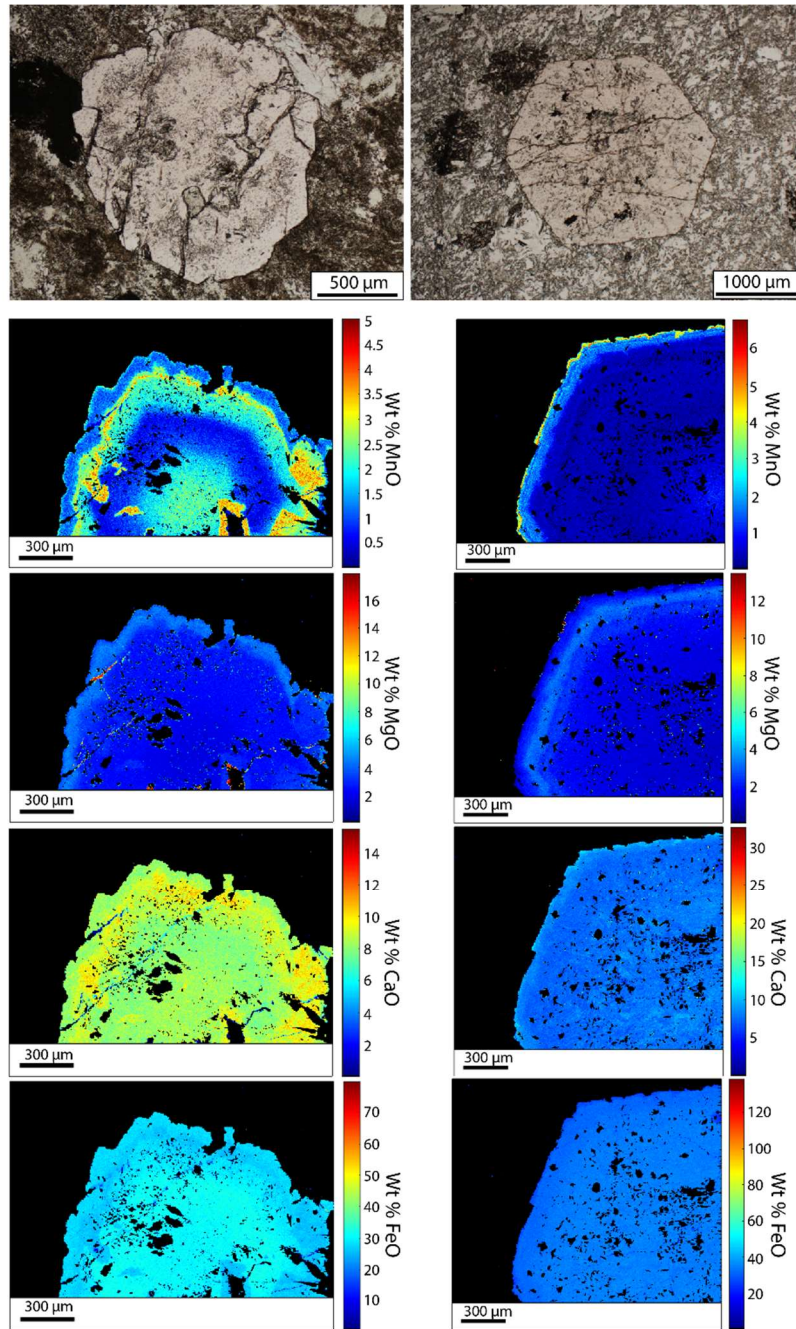


Figure 4.16: X-ray element maps for MVE12-66-1.5 (left) and MVE12-66-7.5 (right). Most element maps have become mildly obscured due to the introduction of error for measure of garnet wt. % oxide due to the inclusion small pixel-scale measurements of Mg, Ca, and Fe bearing phases (e.g., omphacite and phengite) into the calculations for wt. % oxide for garnet. Therefore, x-ray element maps for MnO provides the best glimpse into the chemical zoning in garnet for these samples as there are no Mn bearing phases that were unintentionally included in the calculations for wt. % oxide for garnet.

Garnet sample MVE12-66-1.5 has a very distinct chemical zoning that is easiest to see with regards to MnO (Figure 4.16) (Bradley et al. in preparation). This sample appears to be an at or near central cut of garnet as indicated by the zoning pattern of MnO, with a higher concentration of Mn in the core of the garnet. The most unusual portion of this garnet sample can be seen in the ~200-300 μm closest to the rim, wherein there is an increase and subsequent decrease of MnO in an irregular pattern that does not follow the current grain boundary of the garnet. CaO follows a similar pattern to MnO, though somewhat obscured. MgO is lower in concentration towards the core, with a narrow band of increased concentration that follows the rim of the garnet. FeO has a higher concentration in the core, and a lower concentration towards the rim with the core and rim having separate consistent concentrations. The secondary garnet that has been identified in other research (Bradley et al. in preparation) and is seen as an increase of MnO on the right-hand side of the garnet, shows as a decrease in FeO that does not match the core compositions of FeO of the host garnet.

The x-ray element maps of MVE12-66-7.5 (Figure 4.16) show a very different zoning profile than the ones for MVE12-66-1.5. MnO is once again the clearest in showing any variations in chemical zoning, with a subtle increase of MgO at the core that decreases rapidly. When reaching the rim of the garnet, MnO takes on an oscillatory zoning pattern similar to those observed in garnets from this region before (Tsuji-mori et al., 2006a). MgO is lower in the core of the garnet, with a band of increased concentration that is limited to a 100 μm portion that begins ~100 μm from the rim and follows the general boundary of the garnet. CaO shows an unusual irregular zoning and is

consistent with the profile (Figure 4.15). FeO is largely indistinguishable due to anomalous data points obscuring the calculated FeO composition of the garnet.

4.5.2: Trace Element Zoning

Table 4.1: Trace element concentration for MVE12-66-1.4

Element (ppm)	MVE12-66-1.4 Laser Spot Analysis												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Li	0.698	0.646	0.496	0.392	0.573	0.574	0.445	0.595	0.528	0.569	0.385	0.542	0.742
B	b d	1.64	0.56	1.52	b d	0.49	b d	0.96	0.76	b d	1.79	0.48	0.6
Sc	7.74	4.01	4.82	8.7	8.22	8.48	9.07	9.63	8.98	9.24	8.57	7.44	6.59
V	0.784	0.849	0.629	0.642	0.693	0.66	0.649	0.715	0.701	0.724	0.725	0.881	0.968
Cr	0.013	0.004	0.002	0.002	0.002	0.001	0.002	0.001	0.002	0.002	0.002	0.002	b d
Co	0.054	0.047	0.046	0.046	0.044	0.041	0.041	0.041	0.036	0.036	0.036	0.033	0.03
Sr	0.009	0.14	0.081	0.034	0.05	0.044	0.016	0.034	0.049	0.05	0.058	0.096	0.209
Y	354.82	177.58	28.62	19.9	13.65	12.22	15.88	21.63	24.43	27.82	26.87	40.26	31.7
Zr	0.224	2.83	0.366	0.437	2.72	0.47	3.87	0.527	0.38	0.436	1.237	0.348	0.41
Mo	2.36	1.94	0.664	0.442	0.58	0.577	0.571	0.531	0.682	0.997	1.157	1.096	0.95
Ba	b d	0.030	0.027	0.026	0.013	0.019	0.006	b d	0.027	0.038	0.05	0.047	0.095
Ce	0.01	0.006	0.013	0.002	0.003	0.008	0.007	0.007	0.011	0.01	0.006	0.012	0.024
Pr	b d	0.0451	0.061	0.055	0.019	0.053	0.015	0.042	0.05	0.033	0.049	0.071	0.022

Table 4.2: Trace element concentration for MVE12-66-1.5

Element (ppm)	MVE12-66-1.5 Laser Spot Analysis										Inclusion
	1	2	3	4	5	6	7	8	9	10	
Li	b d	0.71	0.249	0.57	b d	0.274	0.43	0.98	1.19	0.71	0.94
B	1.56	1.5	0.66	0.74	b d	0.77	3.09	b d	1.01	b d	0.94
Sc	9.92	4.79	3.02	5.41	8.52	8.92	10.04	6.93	7.56	9.65	7.3
V	0.462	0.845	0.806	0.581	0.644	0.823	0.828	0.836	1.118	0.865	1.064
Cr	0.004	0.005	0.002	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.017
Co	0.075	0.04	0.04	0.047	0.046	0.041	0.036	0.033	0.032	0.035	0.037
Sr	0.007	0.099	0.165	0.06	b d	0.162	0.176	0.226	0.47	0.126	0.016
Y	30.15	374.02	84.49	22.43	13.46	15.5	34.63	39.72	45.75	57.47	723.89
Zr	0.316	0.145	0.481	0.453	0.295	0.414	b d	0.506	0.225	0.398	0.163
Mo	0.202	0.927	0.814	0.201	0.326	0.315	0.43	0.765	0.717	0.548	1.27
Ba	0.015	0.022	0.077	b d	b d	0.126	0.058	0.112	0.149	b d	0.092
Ce	b d	b d	0.013	0.028	0.017	0.007	0.012	0.018	0.063	0.018	b d
Pr	0.047	0.065	0.068	0.021	0.026	0.079	0.125	b d	0.097	0.025	0.138

Trace element zoning for garnet samples in MVE12-66-1 show some variation between samples (Figure 4.17; Tables 4.1 and 4.2). Rare earth element concentration profiles for these samples are described in Chapter 2. Though not all trace elements show identifiable trends, some do show zoning. Sc for both samples shows a trend of steady

increase in concentration from core towards the rim that is disrupted between 175 and 300 μm from the rim. At this point, both profiles show a decrease in Sc from ~ 8.5 ppm to as low as 3.02 ppm before increasing again towards the rim. Co also has a defined zoning marked by a gradual increase from core to rim, with a marked increase at the rim in MVE12-66-1.5. V also is slightly zoned, with a subtle increase at the core that decreases heading outward from the core before increasing 100-200 μm from the rim and a lower concentration at the rim. Cr, while particularly low in concentration, does show an increase of 0.009 ppm at the rim. Sr shows a higher concentration at the core of garnet with a decrease outward from the core, interrupted by an increase and decrease in concentration zoning in the ~ 200 μm region of the rim of garnet. Y follows a similar pattern to those of heavy rare earth elements (HREEs) and medium rare earth elements (MREEs) as might be expected for garnet (Moore et al., 2013).

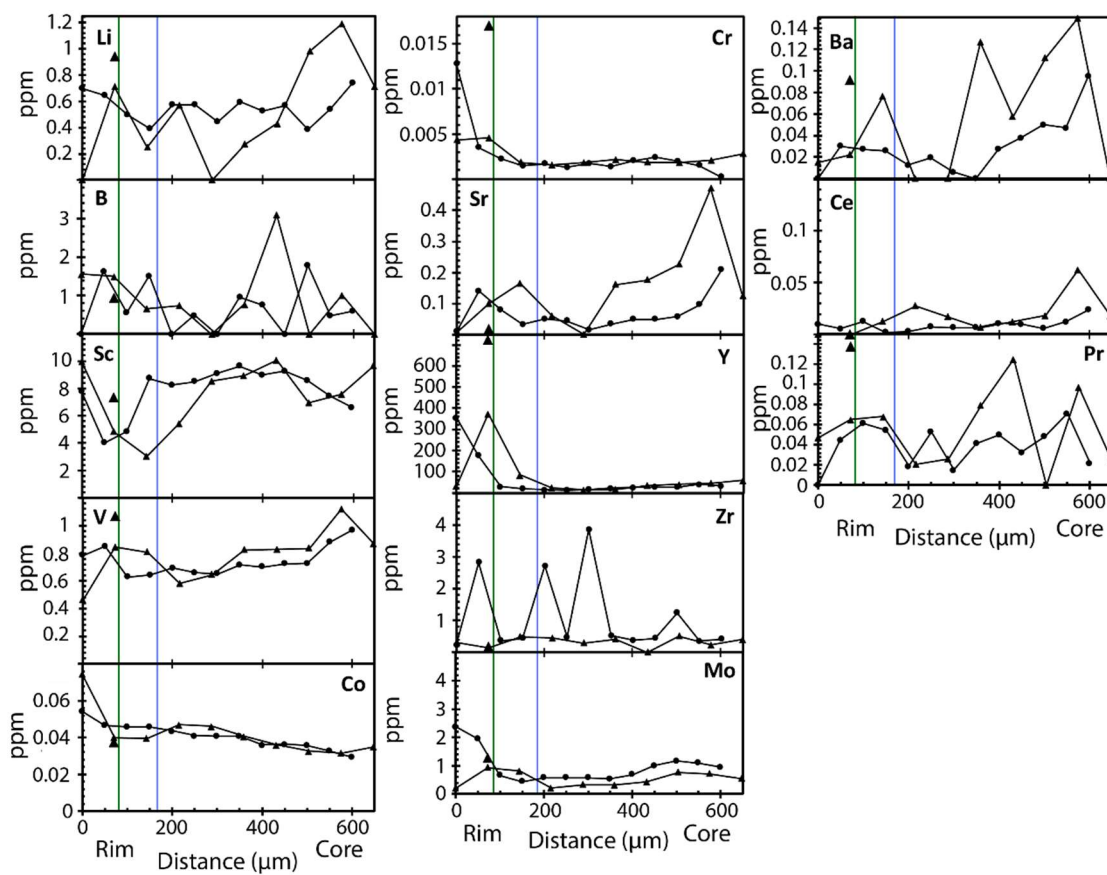


Figure 4.17: Trace element profiles for garnet from MVE12-66-1. Triangle marks are garnet sample MVE12-66-1.5, and circle marks are MVE12-66-1.4. All profiles are plotted from rim on the left to core on the right. The blue line represents where XSps increases, and the green line represents where XSps decreases near the rim.

Table 4.3: Rare Earth Element concentrations for garnet in MVE12-66-7.3

Element (ppm)	MVE12-66-7.3 Laser Spot Analysis															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Nd	b d	b d	0.269	0.282	0.332	0.36	0.402	0.41	0.45	0.291	0.377	0.44	0.37	0.47	0.39	0.48
Sm	3.74	4.75	5.08	8.52	9.63	11.44	10.42	10.7	10.4	10.47	8.84	11.77	12.63	9.69	13.72	11.99
Eu	15.4	16.63	17.31	23.61	26.85	29.32	25.49	27.83	26.8	25.96	23.15	30.98	29.63	23.43	33.07	29.85
Gd	21.92	30.74	33.15	45.04	51.33	50.83	43.78	47.1	51.48	48.57	39.35	49.55	49.91	37.77	53.42	47.84
Tb	42.47	49.68	43.92	49.55	58.48	48.3	35.65	38.78	46.71	46.91	38.3	42.64	41.69	33.07	45.02	39.94
Dy	44.13	53.27	42.69	46.47	56.16	44.21	28.18	28.88	38.77	39.35	32.71	31.47	34.31	27.41	36.42	32.26
Ho	34.52	42.44	35.72	41.49	51.17	40.04	22.99	23.46	31.6	33.87	27.63	21.63	27.26	22.39	29.43	26.3
Er	28.45	34.77	30.18	39	48.56	37.46	20.13	20.65	27.46	29.57	25.26	15.35	23.64	20.28	26.72	24.48
Tm	26.21	31.09	27.59	34.78	45.39	34.71	19.03	19.04	24.55	27.92	23.5	11.6	21.09	17.7	24.01	21.34
Yb	24.56	25.23	24.71	30.8	40.12	31.91	16.55	16.22	20.88	24.17	20.02	8.75	17.67	15.24	20.37	18.96
Lu	28.02	29.67	28.65	32.26	42	33.5	17.54	17.1	21.82	24.7	21.39	7.72	17.79	16.04	21.04	19.17

Table 4.4: Rare Earth Element concentration for garnet in MVE12-66-7.5

Element (ppm)	MVE12-66-7.5 Laser Spot Analysis															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Nd	0.241	0.726	0.294	b d	1.931	0.367	1.097	0.435	1.556	3.81	9.61	1.281	11.01	3.37	0.742	0.409
Sm	4.53	8.59	12.21	6.17	13.28	6.41	8.34	13.27	13.4	15.83	26	13.33	30.29	20.25	17.55	8.66
Eu	17.18	26.35	32.85	23.72	29.83	18.62	20.89	28.27	29.77	34.77	45.18	31.99	63.29	51.66	53.35	26.53
Gd	28.06	49.89	54.55	48.34	44.09	31.54	31.42	36.7	38.09	42.88	56.01	39.76	77.33	64.38	77.87	38.49
Tb	42.76	53.83	50.88	49.66	47.93	28.11	26.27	25.55	25.76	28.95	38.06	28.95	55.88	51.22	62.19	30.58
Dy	44.16	47.94	39.25	38.85	38.75	22.9	21.83	17.97	15.74	19	26.98	20.14	37.88	30.94	41.81	19.54
Ho	32.92	42.36	33.96	37.05	31.63	19.12	18.3	16.3	14.23	15.84	19.71	15.9	29.66	21.68	26.65	13.85
Er	28.79	38.19	30.56	27.71	26.36	15.4	16.59	12.48	11.47	13.87	17.92	13.24	25.05	17.41	21.35	10.74
Tm	24.96	35.87	24.24	22.69	25.3	13.89	12.82	11.12	9.26	12.25	14.62	12.1	18.86	12.86	16.24	8.77
Yb	22.86	31.19	22.21	22.63	20.69	11.99	11.45	8.29	9.08	10	12.91	11.85	20.5	12.66	14.03	7.75
Lu	28.45	32.09	24.81	26.64	19.49	12.76	11.46	10.68	9.49	9.44	16.56	12.01	21.26	11.98	15.21	7.54
Hf	0.681	0.263	0.225	b d	b d	0.236	0.719	0.576	6.75	0.174	0.635	0.183	0.315	25.83	0.544	0.781

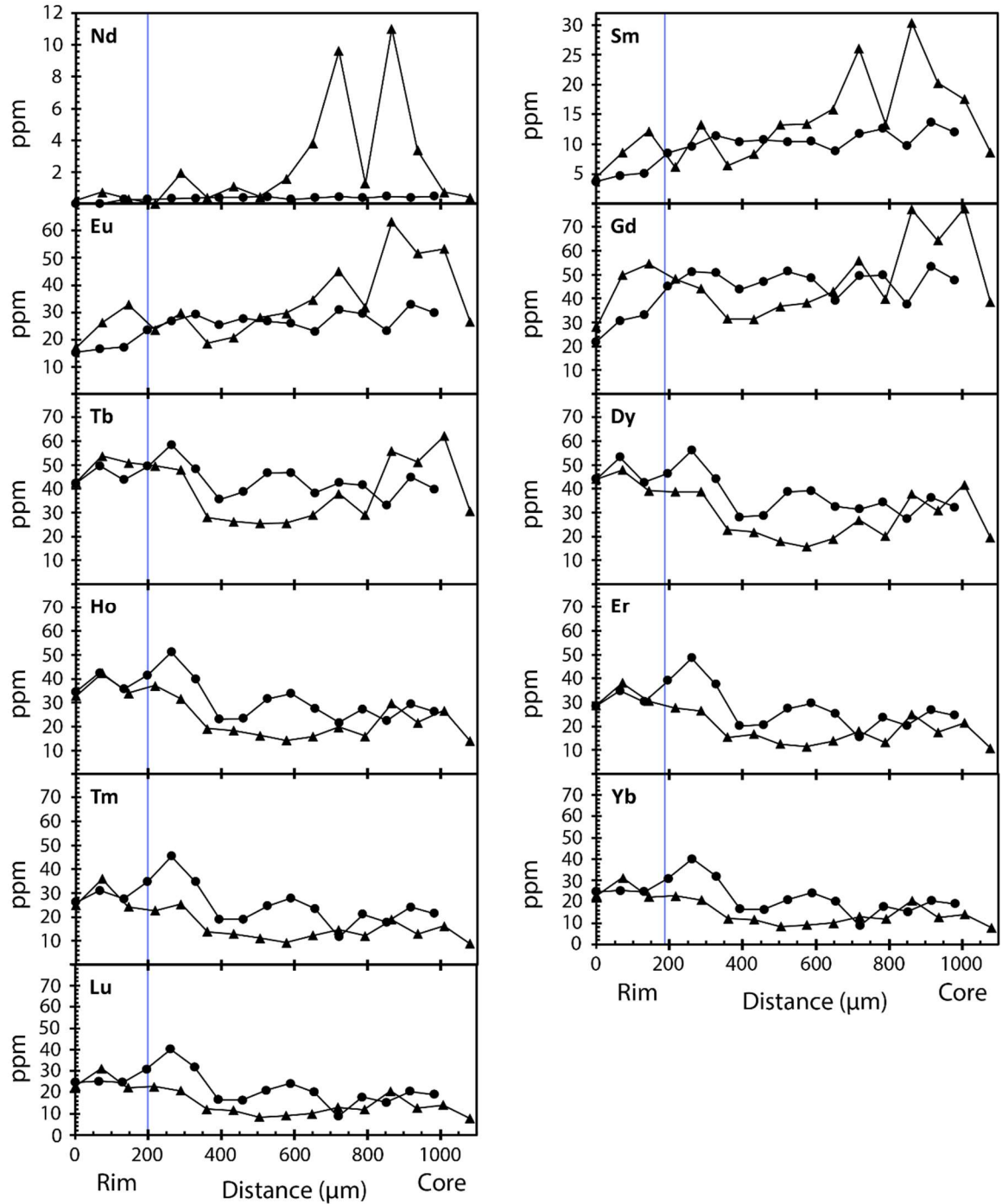


Figure 4.18: Combined rare earth element profiles for MVE12-66-7.3 (circle) and MVE12-66-7.5 (triangle). Highly irregular zoning in MVE12-66-7.5 from 720-864 μm from the rim is likely due to inclusions. The blue line coincides where XSps and XGrs begin to increase and XPrp begins to decrease.

Rare earth element compositions for garnet sample MVE12-66-7.3 (Figure 4.18; Table 4.3) are irregular, with HREEs showing an oscillatory zoning with a general increasing trend from core to rim, there are five separate peaks to these oscillations that occur at 917 μm , 786 μm , 589 μm , 262 μm , and 65 μm from the rim. LREEs shows a steady decrease in concentration until ~ 150 μm from the rim, where decrease is sharp. This zoning is particularly marked by Nd, which decreases from 0.269 ppm to below detection 65 μm from the rim.

Rare earth element zoning for MVE12-66-7.5 (Figure 4.18; Table 4.4) follow a similar pattern observed for garnet in other eclogite samples from this region, with an increase of HREEs towards the rim of garnet but missing a significant central peak which is instead marked by a subtle, gentle increase of HREEs at the core. LREEs are oscillatory with recorded Nd localized concentrations of 9.61 ppm and 11.01 ppm and concentrations of Sm at the same locations of 26 ppm and 30.29 ppm. Discounting these two anomalously high spot analyses, Sm and Nd both display a general decreasing trend from core to rim.

Table 4.5: Trace element concentrations for garnet in MVE12-66-7.5

Element (ppm)	MVE12-66-7.5 Laser Spot Analysis															
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Li	0.47	0.32	b d	0.51	0.55	2.11	1.82	0.29	0.47	b d	0.21	1.81	0.39	0.165	0.68	2.02
B	0.32	b d	0.72	0.45	b d	b d	b d	1.56	b d	0.34	b d	0.71	b d	2.31	b d	b d
Sc	11.7	5.47	4.96	5.43	3.98	4.05	4.69	5.29	4.86	3.8	4.11	4.11	4.87	4.18	5.29	4.56
V	0.361	0.489	0.557	0.566	0.569	0.727	0.752	0.701	0.685	0.571	0.642	0.904	0.677	0.667	0.745	0.933
Co	0.063	0.109	0.07	0.055	0.045	0.031	0.031	0.036	0.032	0.026	0.028	0.023	0.029	0.029	0.03	0.0213
Sr	0.002	0.63	b d	b d	3.6	0.465	1.335	0.67	0.869	1.92	5.14	0.768	6.07	1.308	0.62	0.322
Y	39.36	46.76	37.2	37.15	32.14	19.89	19.22	15.88	14.35	16.04	21.85	16.59	30.54	23.23	30.13	15.36
Zr	b d	0.159	0.389	0.513	0.289	0.182	0.136	0.206	7.47	0.067	0.269	0.156	0.317	25.47	0.355	0.213
Nb	0.027	0.052	b d	0.096	b d	0.022	b d	0.114	b d	b d	0.087	b d	0.09	b d	0.029	0.0223
Mo	0.497	0.26	b d	0.408	0.246	b d	0.174	0.154	0.037	0.184	b d	0.073	0.165	0.301	0.456	0.2
Ba	0.023	1.006	0.054	b d	11.97	0.128	18.76	40.4	16.69	18.76	27.05	0.594	1.898	b d	0.164	0.0743
La	0.032	0.047	b d	b d	0.683	0.044	0.316	0.026	0.38	1.296	4.7	0.345	5.56	1.277	0.148	0.0703
Ce	0.01	0.107	0.013	b d	0.786	0.026	0.389	0.028	0.605	1.962	6.59	0.508	7.29	1.841	0.216	0.0665
Pr	0.067	0.168	0.144	b d	1.405	0.123	0.618	0.078	0.86	2.99	8.58	0.808	9.19	2.7	0.303	0.123

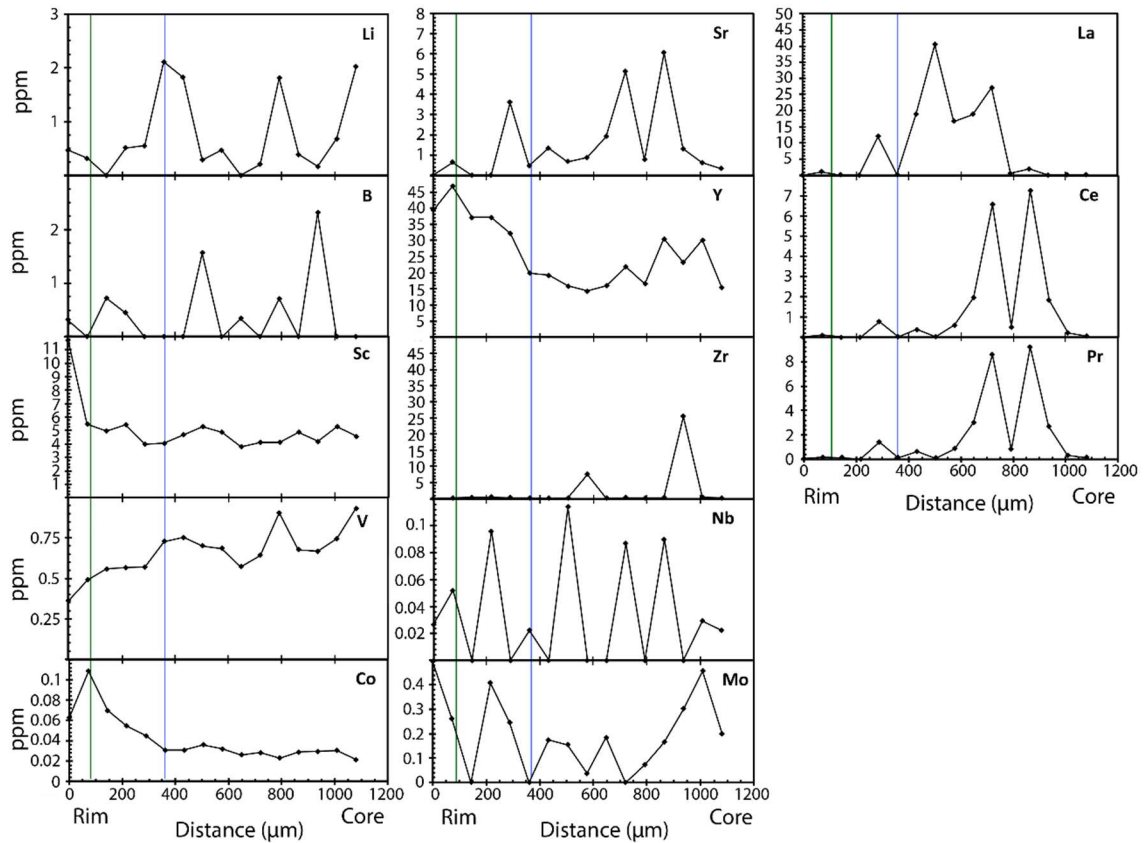


Figure 4.19: Trace element concentration zoning for MVE12-66-7.5. The abundance of tiny inclusions in this sample makes identifying trends difficult. Overall, there is more Sr in this sample than in the previous eclogite samples, which is in line with a lack of Sr in the matrix during garnet growth, which is supported by its absence as inclusions in garnet. The blue line coincides with an increase of XPrp, the green line coincides with a decrease in XPrp, and an increase in XSps and XGrS.

Trace element zoning for MVE12-66-7.5 is highly variable (Figure 4.19: Table 4.5), with only a few elements showing a discernable trend: Sc, V, Co, and Y. Sc has a slightly oscillatory zoning throughout much of the core of the garnet, with concentrations ranging from 3.8 ppm to 5.43 ppm until the rim-most concentration of 11.7 ppm. V has a general trend of decreasing concentration from core to rim, with an oscillatory zoning profile that has three defined peaks at 1080 μm , 792 μm , and 432 μm from the rim that measure 0.933 ppm, 0.904 ppm, and 0.752 ppm, respectively, with a decrease at the rim

that begins at 144 μm from the rim at 0.557 ppm, decreasing to 0.361 ppm at the rim. Co has very well-defined zoning that is slightly oscillatory throughout the core of garnet, before beginning to increase at 360 μm with a concentration of 0.031 ppm and increasing to 72 μm from the rim with a concentration of 0.109 ppm, before decreasing to 0.063 ppm at the rim. Y zoning follows that of HREEs at similar concentrations.

Table 4.6: Trace element data for lawsonite for MVE12-66-7

Element (ppm)	1	2	4	8	16	17
Li	0.94	1.17	bd	0.47	0.182	bd
B	23.78	bd	bd	6.12	1.09	0.22
Sc	0.653	0.392	0.072	0.517	0.148	0.112
V	3.39	4.33	4.5	4.49	6.8	4.98
Cr	bd	bd	bd	bd	bd	bd
Co	0.003	0.001	bd	0.002	bd	bd
Ni	bd	bd	0.001	bd	bd	bd
Cu	bd	bd	0.014	0.088	bd	bd
Sr	547.7	704.09	325.88	704.49	372.07	388.09
Y	9.61	4.14	30.45	3.4	174.09	57.85
Zr	0.754	0.498	0.551	bd	0.227	0.103
Nb	60.17	20.87	0.171	1.98	bd	0.061
Mo	bd	1.08	0.46	bd	bd	bd
Ba	1.49	2.06	0.352	1.08	0.116	0.734
La	158.85	215.07	178.6	238.55	632.55	240.88
Ce	175.25	220.06	174.79	264.76	823.83	308.14
Pr	238.23	277.32	195.24	305.69	1103.64	400.89
Nd	273.34	282.98	196.14	326.63	1255.98	432.46
Sm	263.22	267.05	146.83	253.49	942.97	319.72
Eu	189.5	210.26	122.68	209.17	312.14	132.96
Gd	99.47	98.46	67.56	116.1	834.35	249.64
Tb	41.31	37.03	33.76	34.42	419.52	127.12
Dy	19.81	13.86	28.02	8.88	258.62	75.61
Ho	11.06	5.61	30.61	5.38	170.03	56.79
Er	6.95	3.82	34.95	4.5	92.18	37.87
Tm	8.47	bd	26.68	0.59	30.69	19.25
Yb	6.51	1.82	25.87	0.6	17.46	11.53
Lu	1.4	3.19	23.84	1.75	16.11	10.63

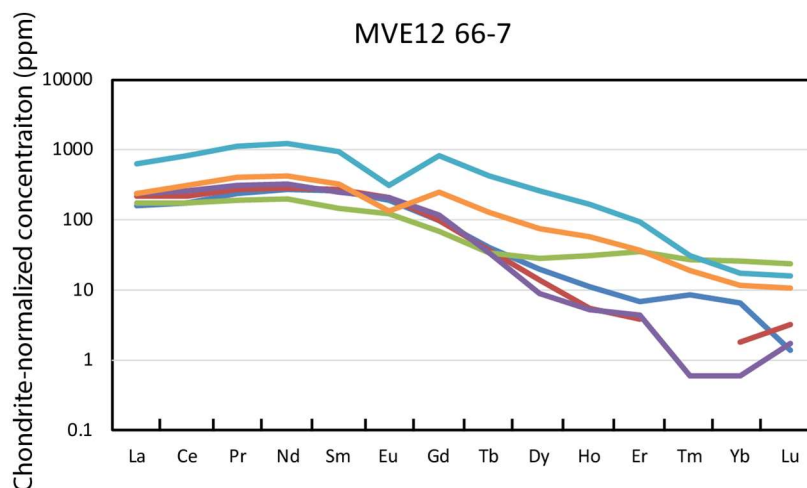


Figure 4.20: REE diagram for lawsonite for MVE12-66-7. Lawsonite in MVE12-66-7 can be found preserved as inclusions in titanite, rather than as inclusions in garnet, suggesting that this lawsonite may have grown after garnet growth, but before retrograde titanite formation. Lawsonite in this sample is substantially more concentrated in LREEs than the lawsonite in MVE12-66-4.

Lawsonite samples for MVE12-66-7 (Figure 4.20; Table 4.6) are found as inclusions in titanite and are not well-preserved in other areas of the eclogite except in veins. Most lawsonite follows the same general elemental preferences, with a significant amount of Sr and high concentrations of LREEs, with one sample containing a very high concentration (Table 4.6). Another mineral that is a repository for trace elements is phengite (Table 4.7), which is rich in B and Ba.

Table 4.7: Trace element compositions for phengite in MVE12-66-7

Element (ppm)	3	5	6	7
Li	3.51	2.52	2.5	2.21
B	124.21	86.11	72.8	54.83
Sc	bd	0.154	0.073	0.169
V	1.408	1.441	1.467	1.497
Cr	bd	bd	bd	bd
Co	0.034	0.022	0.021	0.023
Ni	bd	bd	bd	bd
Cu	bd	0.02	0.0129	0.0187
Sr	4.49	2.46	2.12	2.73
Y	0.283	0.147	0.057	0.061
Zr	1.29	1.025	bd	0.319
Nb	bd	0.389	1.216	0.365
Mo	3.58	0.6	0.32	bd
Ba	732.29	762.82	735.29	707.33
La	0.111	0.109	bd	0.049
Ce	0.101	0.051	0.045	0.025
Pr	0.637	0.158	0.464	0.548
Nd	0.668	0.457	0.254	bd
Sm	2.23	0.98	bd	2.56
Eu	2.93	0.31	1.79	0.89
Gd	5.1	bd	3.17	bd
Tb	1.41	1.26	0.24	bd
Dy	1.32	0.303	bd	bd
Ho	1.21	0.68	1.13	0.76
Er	0.667	bd	0.341	0.29
Tm	1.9	bd	1.17	bd
Yb	bd	0.64	bd	0.35
Lu	3.99	1.2	1.43	0.72
Hf	3.07	2.49	1.74	0.66

4.5.3: Age Data

Table 4.8: Sm and Nd element and isotope data for MVE12-66-1

Sample ID	Sample Name	Original Sample Weight (mg)	Sm (ppm)	Nd (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$
17N130A	Garnet	96.82	3.458	6.798	0.3076	0.513137
17N130B	Garnet	95.49	3.499	6.991	0.3026	0.513152
17N131	Leachate	12.94	3.005	9.361	0.1448	0.513043
18N13	Bulk	49.8	2.325	7.88	0.1784	0.513035
18N14	Omphacite	48.6	2.303	8.946	0.1557	0.513038
18N15	Lawsonite	1.8	3.675	13.017	0.1707	0.513050

Sm-Nd ages were biased towards a rim age by picking exclusively inclusion-free garnet, which is found primarily at the rim of garnet within this eclogite sample. Multiple phases were analyzed to create an isochron: lawsonite, garnet, clinopyroxene, whole rock, and leachate from early garnet leaching. This sample, MVE12-66-1, has produced the youngest age thus measured for a lawsonite eclogite from the South Motagua Suture Zone at 107 ± 35 Ma. A low mean square weighted deviation (MSWD) and usage of multiple phases makes this age comparable to other Sm-Nd ages obtained in this area (Brueckner et al., 2009). The high error produced by this isochron, however, places this age within error to Sm-Nd ages obtained by Brueckner et al., 2009.

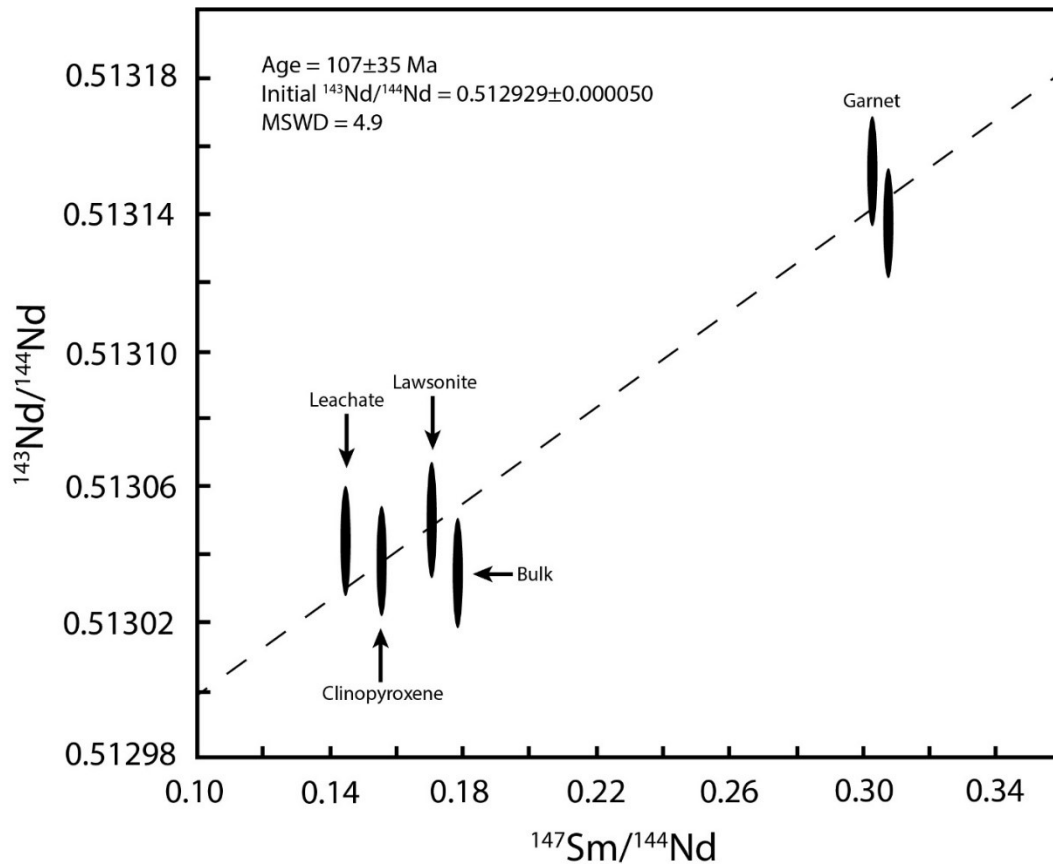


Figure 4.21: Age data for MVE1266-1. Ellipses represent 2σ error. The garnet ellipsis to the right represents garnet population A that experienced an additional leaching step.

4.6: DISCUSSION

4.6.1: Major Element Zoning Variance

Much of the core major element zoning for MVE12-66-1 and MVE12-66-4 is consistent with that expected for prograde-zoned garnet, with a bell-shaped curve for Mn with a high concentration in Mn in the core, and an inverse bell curve for Fe and Mg (Hollister, 1966; Skora et al., 2006). However, for MVE12-66-7, this expected chemical zoning is nearly absent, except for a very subtle increase of Mn in MVE12-66-7.5 (Figure 4.15). While this lack of central peak in nearly all samples in MVE12-66-7 may be an indication of an off-core cut of garnet, it is unlikely that so many garnet samples show

low concentrations in XSps when compared to those in other eclogite samples.

Additionally, the central peak of XSps in MVE12-66-7.5 is very narrow when compared to those in other eclogite samples, so this deviation from the zoning observed in other eclogite samples is likely due to the nature of garnet in this eclogite when compared to other eclogite samples

In many instances, an increase of XSps at the rim of garnet is typically attributed to retrograde processes (e.g., Woodsworth, 1977; De Lima et al., 1995; Kohn and Spear, 2000; Gulbin, 2013), with resorption of garnet resulting in the backwards diffusion of Mn into garnet. However, there is no evidence of this resorption taking place in garnet in any of the eclogite samples. Additionally, diffusion in garnet at these temperatures is negligible to nonexistent (Caddick et al., 2010), so it is unlikely that this zoning is related to backwards diffusion into garnet.

The cause for major element zoning has been described in detail for MVE12-66-1 and MVE12-66-4 in Bradley et al. (In Preparation) and depends on both mineral availability and fluid infiltration during garnet growth to create the unusual zoning of major elements in garnet. As chlorite was present throughout the duration of garnet growth and an absence of any epidote end-members in these samples, it was determined that consumption of this mineral phase to facilitate garnet growth and fluid infiltration to increase intergranular diffusion was responsible for XSps zoning (Banno and Chii, 1978; Tracy, 1982; Inui and Toriumi, 2004; Gardés et al., 2012). In MVE12-66-7, however, XSps is much lower in concentration throughout the core of garnet, and chlorite is not present as inclusions in garnet to the same abundance as in MVE12-66-1 and MVE12-66-

4. Therefore, there must be either another mineral phase present that helps explain the increase of XSps at the rim of garnet in MVE12-66-7, or there must be another process at work.

There are several different minerals that have been suggested as reservoirs of Mn used in garnet formation: Chlorite (Tracy, 1982; Banno and Chii, 1978; Inui and Toriumi, 2004), Mn-bearing epidote (Yang and Rivers, 2002), or Mn-rich ilmenite (Woodsworth, 1977). In MVE12-66-1 and MVE12-66-4, it was determined that chlorite was the most likely source of Mn found in garnet (Bradley et al., In Preparation). For MVE 12 66-7, there are actually several options for sources of Mn, with the most likely being chlorite and clinozoisite through a combination of the reactions: chlorite + epidote + quartz = (Fe-rich) garnet + (Na-Ca) amphibole + H₂O (Konrad-Schmolke et al., 2008), and (Na-Ca) amphibole + epidote = garnet + omphacite + phengite + quartz (Zhou et al., 2014), with ilmenite being less likely as that is more common in pelitic garnet (e.g., Woodsworth, 1977; Schumacher et al., 1999). The combination of these reactions would also explain the abundance of phengite in the matrix. Consumption of these hydrous phases would also release H₂O, increasing rates of intergranular diffusion (Gardés et al., 2012), and would serve as the source for Mn-rich fluids (Moore et al., 2013).

Though it has been suggested that fluctuations in pressure due to seismic events may cause oscillatory zoning through growth and dissolution events (Viète et al., 2018), it is unlikely that this is the cause of the oscillatory zoning in these garnet samples, as there is little petrographic evidence of a seismic event such as fractures that have been sealed afterward during continued garnet growth. Zoning is instead interpreted to be due

to pulses of fluid infiltration due to consumption of hydrous phases during the later stage of garnet growth, which would occur in low temperature conditions (Hernández-Urbe and Palin, 2019). The oscillatory zoning at the rim is not only visible in Mn, but in Ca, and Mg. Increase in Ca at the rim is likely due to consumption of clinozoisite (Hickmott et al., 1987; Yang and Rivers, 2002; Volkova et al., 2014). This increase in Ca and Mg at the rim of garnet could also be facilitated by the reaction: lawsonite + omphacite = pyrope + grossular + quartz + H₂O (Du et al., 2014), which can be seen in veins in the matrix with the crystallization of quartz and new garnet in veins.

4.6.2: Trace Element Zoning Variance

Trace element zoning and their causes for MVE12-66-1 and MVE12-66-4 have been described in detail in Chapter 2. Most notable for trace element zoning in those samples was a zoning in Sr, which is sourced primarily from lawsonite (Table 4.6) (Usui et al., 2007; Martin et al., 2014; Viltale Brovarone et al., 2014; Hara et al., 2018; Fornash et al., 2019), which also serves as a reservoir for LREEs. A decrease of LREEs would be indicative of formation of additional lawsonite, which has been documented in this region (Hara et al., 2018). MVE12-66-7.5 (Figure 4.19) contains more Sr than MVE12-66-1 (Figure 4.17), which is likely due to its' relative lack of lawsonite by comparison, which would have sequestered Sr early, only releasing it during consumption. Oscillations in Sr zoning may be due to fluid pulses during lawsonite consumption, but the extent of this oscillation is obscured due to influence by inclusions on spot analyses. The marked decrease of LREEs at the rim of garnet is likely due to formation of late lawsonite that is preserved as inclusions in titanite. Y and Sc zoning will be influenced by the breakdown of clinozoisite in favor of garnet (Hickmott et al., 1987; Yang and Rivers, 2002; Konrad-

Schmolke et al., 2008; Volkova et al., 2014), thus formation of clinozoisite would result in a decrease of Sc in garnet while an increase in Sc in garnet would indicate the loss of clinozoisite. HREEs are typically sequestered into the core of garnet early during garnet nucleation and growth (Skora et al., 2006; Volkova et al., 2014). This high concentration of HREEs in the core of garnet is not well preserved, but there is a subtle higher concentration in HREEs in the core of MVE12-66-7.5. Most notably, there is an increase of HREEs at the rim of garnet in the same zone wherein there is an increase of Mg, Mn, and Ca, and thus these zones of increase in concentration are likely related, with the consumption of clinozoisite and chlorite late in garnet growth allow for an increase in intergranular diffusion due to the release of H₂O during these garnet-forming reactions. Increase in Co in MVE12-66-1 (Figure 4.17) and MVE12-66-7 (Figure 4.19) and Cr in MVE12-66-1 in garnet may be due to influence from serpentinite (Sorensen et al., 2010), with an increase in intergranular diffusion due to fluid infiltration, there may be an increase of influence from the *mélange* bordering the subducting slab.

4.6.3: A Complex History

One possible explanation for this odd chemical zoning would be through metasomatic processes via the introduction of fluids from the subducting slab into the *mélange*, altering these HP/LT metamorphic rocks after peak metamorphism and allowing for secondary growth during the retrograde path (e.g., Hoscheck, 2001; Ota et al., 2004; Tsujimori et al., 2006b), or during a secondary prograde path (Figure 4.22) (e.g., LeBayon et al., 2006; Kabir et al., 2010; Blanco-Quintero et al., 2011; Herwartz et al., 2011; Regis et al., 2014; Cheng et al., 2016; Li et al., 2016; Liati et al., 2016) fueled by multicyclicity in the subduction zone (Brueckner, 2004; Brueckner, 2006; Rubatto et

al., 2011; Wakabayashi, 2012). This phenomenon has been observed in trace element zoning in lawsonites in Type-II eclogites from this region, showing two distinct growth stages for lawsonite (Hara et al., 2018). The primary drawback of applying this model to these eclogites is that these eclogites do not match the description of Type-II eclogites and instead are Type-I eclogites, lacking the preservation of the second-stage eclogite-facies recrystallization.

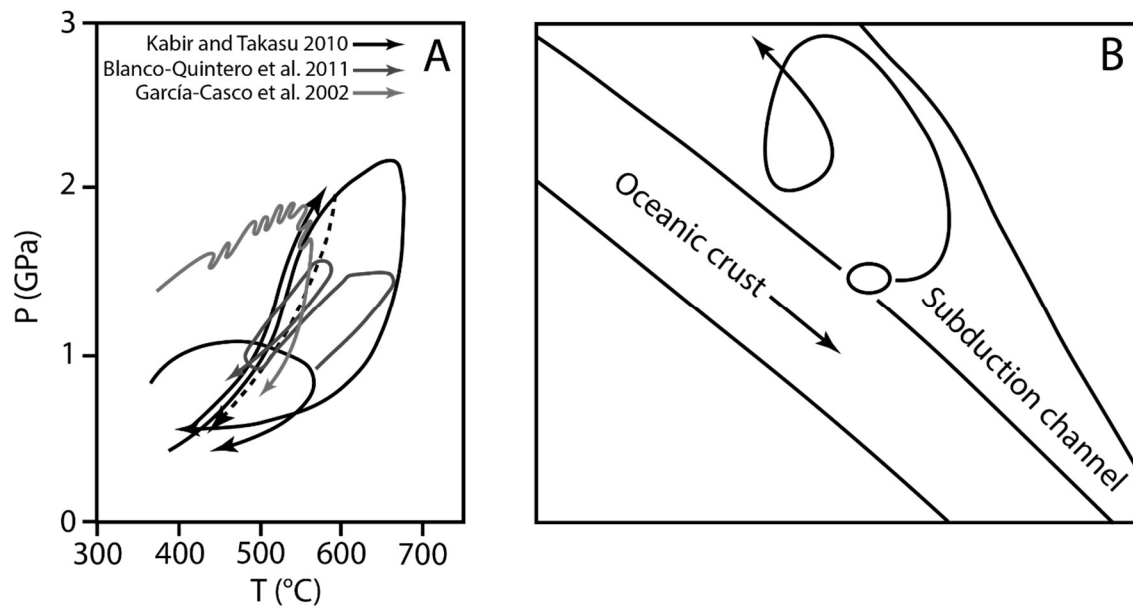


Figure 4.22: A) Combined P-T paths showing multiple prograde paths calculated for eclogite in a variety of subduction zones reproduced from García-Casco et al. (2002), Kabir and Takasu (2010), and Blanco-Quintero et al. (2011). B) Schematic of subduction zone with multi-cyclic subduction and exhumation revised from Li et al. (2016).

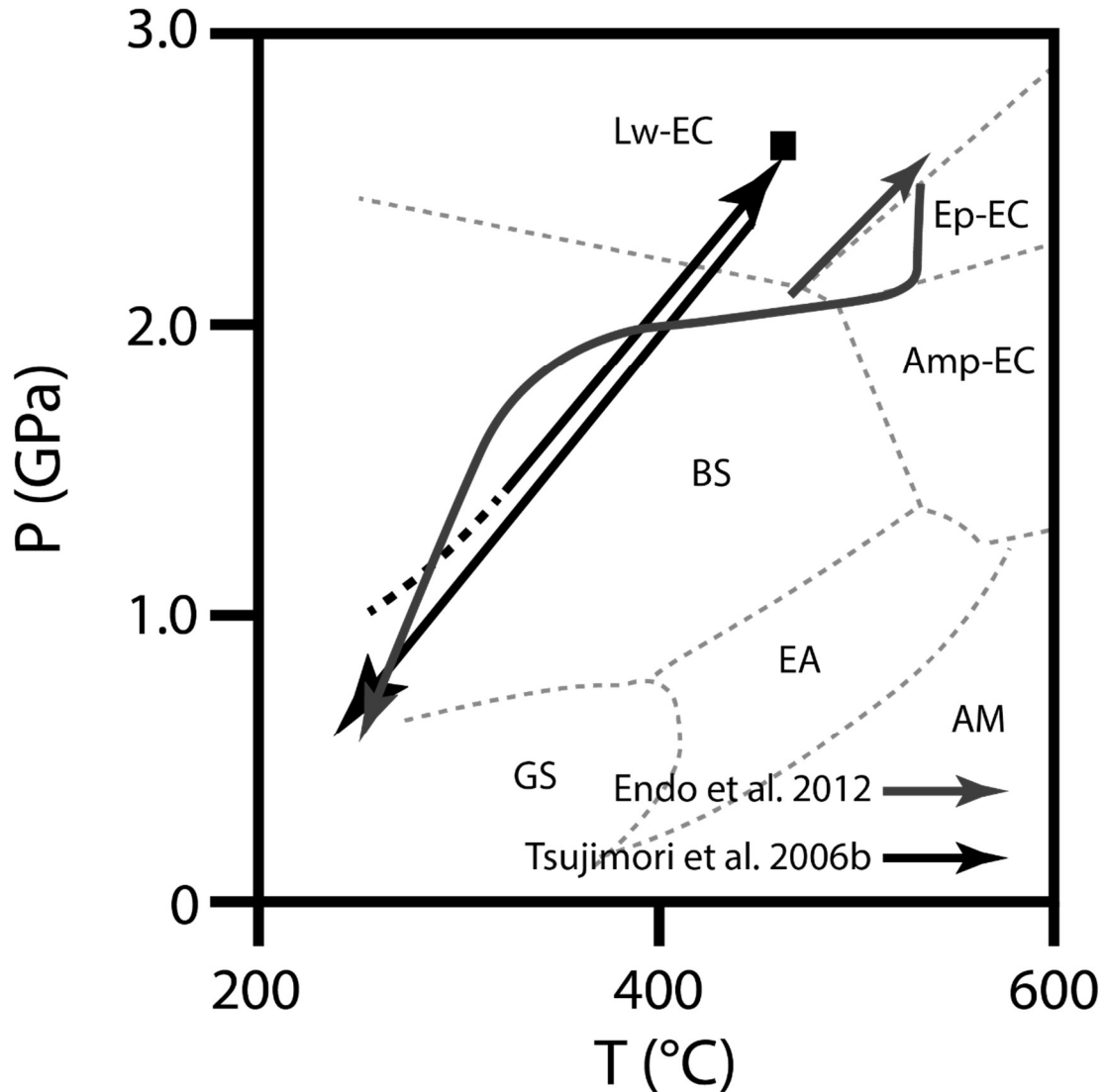


Figure 4.23: Calculated P-T path from Tsujimori et al. 2006b and Endo et al. 2012. Large square indicates peak P-T conditions for Tsujimori et al., 2006b. Metamorphic facies and their abbreviations are from Liou et al. (2004).

As the chemical zoning observed in MVE12-66-1 and MVE12-66-4 is substantially different from those seen in MVE12-66-7, it is very likely that they experienced different metamorphic histories, and possibly different P-T histories as well. Currently, there are two competing P-T paths that have been calculated for the South Motagua Suture Zone eclogites (Figure 4.23) (Tsuji-mori et al., 2006b; Endo et al., 2012).

In comparing these two eclogite populations, one of the most obvious compositional variances is the difference in the concentration and zoning of Mn throughout all garnet samples. In MVE12-66-1 and MVE12-66-4, there is a bell-shaped curve in Mn concentration, which is a typical prograde-zoned pattern (Hollister, 1966; Konrad-Schmolke et al., 2005; Skora et al., 2006; Caddick et al., 2010). In MVE12-66-7, however, this central peak for Mn is largely missing. It is well documented that Mn facilitates garnet nucleation and growth at lower temperatures (Mahar et al., 1997, Inui and Toriumi, 2004, Konrad-Schmolke et al., 2005). As garnet in MVE12-66-7 is substantially lower in concentration in Mn when compared to other garnet samples in other eclogites in this region, it is likely that they had to nucleate and grow at higher temperature than those from MVE12-66-1 and MVE12-66-4. With this portion of garnet history likely occurring at higher temperatures and the variability of eclogite from this region not just chemically, but petrologically, it is possible that both of these P-T histories may have occurred and the P-T path produced is dependent on the sample analyzed and may not be identical from sample to sample.

4.6.4: Providing Constraints on Timing of Peak P-T

Sm-Nd garnet geochronological analysis of this eclogite produced an age of 107 ± 35 Ma (Figure 4.21), which is the youngest age recorded thus far for lawsonite eclogite from the South Motagua Suture Zone, as the temperature history of this subduction zone places it well below the closure temperature of Sm-Nd in garnet (Mezger et al., 1992), this age is representative for peak P-T conditions for garnet. This age is close to that of a Lu-Hf garnet age of 101.8 ± 3.1 Ma that was recorded for an eclogite north of the

Motagua fault (Malodando et al., 2018). What is particularly unusual for this region is that jadeitite from this region was initially determined to have formed after eclogite. Sm-Nd garnet geochronology suggests lawsonite eclogite formed from 140-120 Ma (Brueckner et al., 2009) and $^{40}\text{Ar}/^{39}\text{Ar}$ phengite ages placing jadeitite formation at 125-113 Ma (Harlow et al., 2004). This was initially paired with P-T calculations that showed a simple subduction and exhumation history for this region that placed eclogite formation from 300-480 °C and 2-2.5 GPa (Tsujimori et al., 2004; Tsujimori et al., 2006b).

Though this age is not directly in line with ages produced for Sm-Nd in garnet in prior studies (e.g., Brueckner et al., 2009), it is biased towards the youngest portion of the garnet, as inclusion-free garnet was hand-picked for analysis and the only portion of the garnet that was consistently inclusion-free was the rim. However, based on the spread of Sm-Nd data for non-garnet samples (Figure 4.21) garnet likely grew in an open system rather than the typically assumed closed system, making this age suspect. Additionally, this age is still within error of other Sm-Nd dates produced for this region, making it possible that this age is actually not a reflection of a protracted garnet growth history and is instead affected by open system behavior during the later stages of garnet growth.

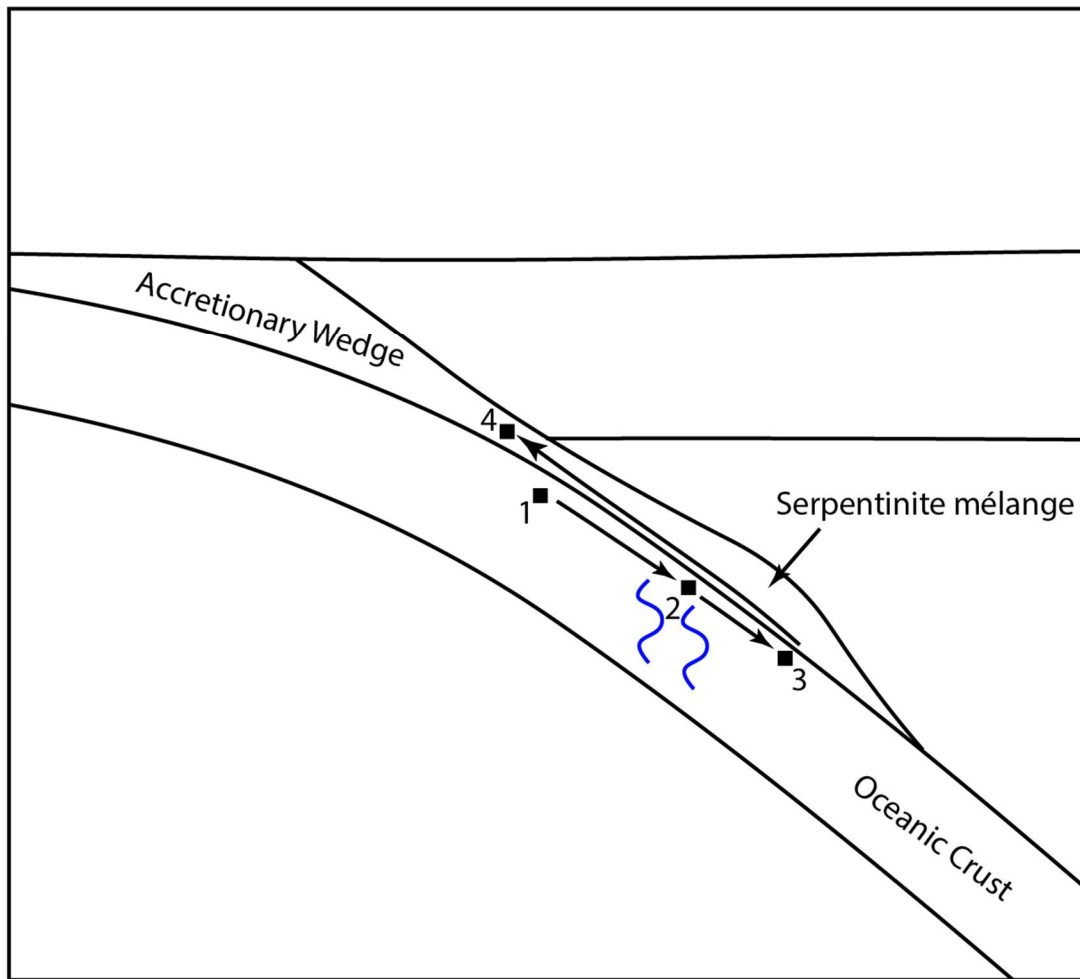


Figure 4.24: Model for subduction and exhumation of lawsonite eclogite for the south Motagua suture zone. 1) Eclogitization begins ~ 120 Ma (Brueckner et al. 2009) at 300 °C and 1.1 GPa (Tsujimori et al. 2006b). 2) Partway through subduction, garnet formation results in consumption of hydrous minerals, resulting in fluid infiltration into eclogite that brings in new material and increases intergranular diffusion allowing for additional garnet growth and nucleation. 3) Peak P-T conditions for lawsonite eclogite at 480 °C and 2.6 GPa (Tsujimori et al., 2006b). 4) Exhumation of lawsonite eclogite is nearly complete, with lawsonite coexisting with jadeitite within exhumed serpentinite mélange and mixed into the accretionary wedge awaiting final exhumation at 24 Ma (Francis, 2005; Simon-Labrie et al., 2013).

It has been determined that these eclogites experienced a very complex, multi-stage prograde history (Figure 4.24) (Chapter 2), which is punctuated by periods of fluid infiltration during subduction that facilitated garnet growth and nucleation. Based on

textural analysis of inclusions in garnet, it is likely that garnet growth rate varied throughout garnet growth, meaning that slower garnet growth would result in regions that are inclusion-poor (Yang and Rivers, 2002). Variability of growth rate has also been observed in other regions based on geochronological analyses of garnet within individual garnet samples (Dragovic et al., 2015). This variability in growth rate would coincide with pulses of fluid infiltration, which would allow garnet to grow quickly with an abundant supply of garnet-forming components.

4.7: FURTHER AVENUES OF RESEARCH

Over the course of this study, there have been a wide variety of avenues explored to explain the unusual chemical zoning of garnet in these lawsonite eclogites from the Carrizal Grande region of Guatemala (Bradley et al., in preparation). I have examined garnet samples with regards to petrology, major element zoning, trace element zoning, crystal size distribution, and even Sm-Nd geochronology. While I have arrived at a reasonable conclusion, more evidence is required in order to make for a truly robust story. The samples examined over the course of this study were all different in several aspect of their petrology and many of these samples were unable to be given full examination due to their unsuitability for geochronological analysis due to the severely retrogressed nature of the garnet in those samples that destroyed portions of the garnet that I have been focused on through the duration of this study. It is therefore recommended that, even though these samples may be unsuitable for geochronological analysis, future research into what chemical zoning may be preserved would be valuable. From sample to sample, garnet analyzed in this study and others, it has been seen that

oscillatory zoning of garnet can take on many appearances (e.g., Tsujimori et al., 2006a; Bradley et al., in preparation).

Dating lawsonite as well as garnet in these eclogites would provide constraints on timing of formation of both garnet and multiple generations of lawsonite (Mulcahy et al., 2014). Lu-Hf has not been used in these samples so far and is a geochronometer that both of these minerals have in common. Additionally, if large enough garnet samples were to be found, it would be informative to sample discrete sections of the garnet and date discrete growth bands in garnet to provide constraints on growth rate, as it appears that growth rate in these samples is discontinuous (Pollington and Baxter, 2011; Dragovic et al., 2015; Cheng et al., 2016). As an extension of this, getting trace element abundances would be useful. In order to get better resolution trace element zoning, further analyses taken for these samples should be taken with a smaller spot size, as the 50 μm spot size made it difficult to avoid influence from inclusions due to the high abundance of trace element rich inclusions that are small and nearly impossible to miss.

4.8: CONCLUDING REMARKS

Lawsonite eclogite from the South Motagua Suture Zone has experienced a complex, multi-stage metamorphic history punctuated by instances of fluid infiltration and discontinuous rates of garnet growth. This multi-stage history is easiest to see in MVE12-66-1 and MVE12-66-4, where a typical prograde chemical zoning is interrupted by an atypical zoning and oscillatory zoning of major elements and trace elements preserved at the rim of garnet. This atypical zoning is interpreted to be due to an increase in intergranular diffusion caused by consumption of hydrous minerals like chlorite,

resulting in an increase of Mn towards the rim due to increasing intergranular diffusion of trace elements. This consumption of hydrous materials released H₂O into the system at periodic intervals, causing the oscillatory zoning that is observed at the rim of garnet in MVE12-66-7. The variability of chemical zoning and petrographical characteristics between eclogite samples suggests that they experienced different prograde histories over slightly different P-T conditions, making it likely that the two competing calculated P-T paths for this region are representative of different eclogite samples, making both P-T paths possible in the same subduction zone.

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APPENDIX A

Table A.1: Major Element Zoning for MVE12-66-1.4

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.7929	8.36	1.1637	29.4626
	15	4.2064	8.5773	0.9731	27.6518
	45	3.6182	8.9646	1.4734	27.5905
	60	3.0397	9.1846	2.6471	27.2632
	75	3.0395	9.3232	2.4935	27.2164
	90	2.4901	8.684	2.1989	28.9494
	105	2.3595	8.3501	2.0375	29.0982
	120	2.3028	8.3505	1.7553	30.1316
	135	2.3692	8.4233	1.7479	30.2763
	150	2.4083	8.3305	1.7734	29.9875
	165	2.3662	8.3536	1.2242	31.0912
	180	2.2507	8.4806	1.1641	31.292
	195	2.3691	8.266	0.6495	31.5127
	210	2.164	8.5131	0.6631	32.2016
	225	2.3642	7.4281	0.5129	33.1239
	240	2.3504	8.3739	0.4727	32.0525
	255	2.2111	9.2168	0.4998	31.4823
	270	2.261	8.3774	0.6672	31.511
	285	2.2604	7.614	0.6665	31.4721
	300	2.1688	8.3629	0.6096	31.6708
	315	2.3062	7.8555	0.6341	32.027
	330	2.2839	8.5559	0.6553	31.2166
	345	2.2064	7.7867	0.6084	32.7893
	360	2.3354	7.5738	0.7369	32.367
	374	2.1776	7.9277	0.8235	32.4303
	390	2.2579	8.171	0.7473	31.7684
	405	2.0813	8.3032	0.8099	31.8163
	420	2.1913	8.1981	0.941	31.7459
	435	2.0761	8.5353	0.6641	31.7411
	465	2.1822	8.0985	0.8747	31.4894
	480	2.0832	8.3314	0.9085	31.6404
	510	1.9157	8.4074	0.9428	31.5857
	525	2.006	8.5126	0.8718	31.472

Table A.1 (cont'd): Major Element Zoning for MVE12-66-1.4

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	540	1.9998	8.7281	1.0626	31.8359
	570	2.0682	8.0441	1.2172	31.5564
	585	2.0314	8.0305	1.2652	31.4828
	600	1.9684	9.1049	1.1259	30.7011
	615	1.8767	8.4686	1.3705	31.4761
	630	2.058	8.562	1.2751	31.3065
	645	1.92	8.4377	1.1546	30.9413
	660	1.7862	8.603	1.337	31.3194
	675	2.0244	8.2577	1.4434	31.9367
	690	1.8747	8.5554	1.4793	31.351
	705	1.7731	8.463	1.373	30.217
	720	1.8157	8.1107	1.5386	31.0975
	735	1.7996	8.5177	1.6726	30.3885
	750	1.9039	8.895	1.6426	29.8668
	765	1.9676	8.3689	1.6374	30.1575
CORE	780	2.0738	8.3175	1.5855	31.6034

Table A.2: Major Element Zoning for MVE12-66-1.5

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.9536	8.7842	1.4047	28.2897
	15	4.0924	8.7957	0.9161	27.534
	30	4.0246	8.5225	0.9802	29.2125
	45	3.6326	9.4226	1.2911	28.1336
	75	2.2701	9.3359	2.1453	27.9868
	90	2.4735	8.649	2.358	28.889
	120	2.3176	8.9705	1.5753	29.5806
	135	2.2496	8.6554	1.2331	30.6622
	150	2.3073	8.3883	0.8708	31.4718
	164	2.1823	8.1416	0.6825	31.8933
	180	2.3179	8.1397	0.5893	32.1561
	195	2.2794	8.3153	0.4612	32.3132
	285	2.147	8.9493	0.8294	30.9758
	300	2.242	8.6007	0.9731	31.7385
	315	2.2154	8.0403	0.9847	31.9799
	330	2.2119	8.0665	0.8328	32.0874
	390	2.3549	8.1772	1.7735	30.2413
	420	1.9443	8.211	1.4316	31.909
	435	1.8311	8.7108	1.4744	29.8936
	450	1.7436	8.2099	1.5465	31.1424
	465	1.7774	8.9376	1.6956	31.1067
	480	1.7628	8.2918	1.7109	30.7873
	495	1.6819	9.0125	1.7104	29.8645
	510	1.7175	8.5479	1.7026	30.9716
	525	1.6852	8.9066	1.8623	30.1274
	540	1.7719	8.0946	1.9242	30.7492
	555	1.6281	8.9705	1.9889	31.0799
	570	1.6467	9.1949	1.8676	30.1477
	585	1.635	8.6995	2.2742	29.9709
	600	1.5221	9.4459	2.1163	29.9993
	615	1.5799	8.816	1.9266	30.7039
	630	1.5717	8.6273	1.8764	30.7709
	645	1.6926	8.5636	2.0864	30.7056

Table A.2 (cont'd): Major Element Zoning for MVE12-66-1.5

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	660	1.5925	8.3617	2.346	30.6833
	675	1.5074	8.7522	1.9723	30.8484
	690	1.475	8.7089	2.1856	30.5275
	705	1.5296	8.3756	2.3121	30.5207
CORE	720	1.6632	8.2499	2.1621	30.5419

Table A.3: Major Element Zoning for MVE12-66-1.6

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.6611	8.5433	1.5324	28.5764
	15	3.9438	8.5656	1.0948	28.4933
	30	4.0091	8.3898	0.9868	28.5271
	45	4.0593	8.8461	1.0655	28.1217
	60	3.6919	9.0244	1.52	27.8522
	75	3.1693	9.262	2.6232	26.7166
	90	2.7649	9.2741	2.8947	27.1646
	105	2.5128	8.8909	2.1884	28.4164
	120	2.4532	8.9408	2.2018	29.976
	135	2.4245	8.9888	1.9795	28.8803
	150	2.3504	8.5354	1.8029	29.7249
	165	2.7661	9.0955	1.7382	28.0119
	180	2.1878	9.2569	1.372	29.7166
	195	2.2992	8.9644	1.5001	30.305
	210	2.1592	8.5341	1.2788	29.968
	225	2.2889	8.6424	1.0854	30.8372
	240	2.602	8.0381	0.8963	30.7259
	270	2.4138	8.1334	0.6372	32.3797
	285	2.3469	7.7847	0.7015	32.9651
	300	2.2459	7.754	0.5624	32.9579
	390	2.1394	8.2048	0.7429	31.9446
	405	2.1915	8.1797	0.8572	31.8118
	421	2.1089	8.5338	0.8745	31.6188
	435	2.1839	8.5577	0.9501	31.737
	450	2.1094	7.8185	0.9813	32.6935
	465	2.0682	8.0931	0.8894	31.4205
	480	2.0765	8.3621	0.9746	31.1483
	495	2.09	8.2696	0.9376	31.6988
	510	1.9918	8.2791	1.0026	31.5449
	525	2.0498	7.9935	1.2548	32.3662
	540	1.9821	8.4279	1.2357	31.3309
	555	2.0687	8.3264	1.1917	31.3422
	570	1.9481	8.6996	1.1942	30.9098
	585	2.008	8.1006	1.2423	31.9717

Table A.3 (cont'd): Major Element Zoning for MVE12-66-1.6

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	600	1.998	8.2058	1.1372	31.4227
	615	1.821	8.7524	1.286	30.9018
	630	1.8392	8.6942	1.4165	31.592
	645	1.9217	8.4249	1.5024	31.4194
	660	1.8985	8.471	1.3948	31.2462
	675	1.924	8.5623	1.3742	31.0872
	720	1.8571	8.8532	1.4558	31.0873
	735	1.8474	7.9953	1.5788	31.4292
	750	1.7389	8.9516	1.3901	31.248
	765	1.8333	8.3073	1.7136	30.5922
	780	1.6847	8.9591	1.5623	30.4593
	795	1.7521	8.2802	1.6629	30.8467
	810	1.8212	8.0472	1.5097	31.0471
	825	1.7976	8.6388	1.6229	30.8039
	840	1.8208	8.6968	1.5854	30.7151
	870	1.717	8.8937	1.6294	30.4424
	900	1.863	8.062	1.5018	31.3343
	915	1.756	8.5543	1.7627	31.0288
	930	1.7064	8.8905	1.659	30.6419
	945	1.6687	8.897	1.6167	30.9876
	990	1.6863	8.8964	1.5694	30.8652
CORE	1020	1.7818	9.0314	1.4071	30.6226

Table A.4: Major Element Zoning for MVE12-66-4-002.1

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.3754	8.1913	1.7297	28.1669
	14	4.0209	7.8403	0.936	28.9841
	28	4.4343	8.1156	0.8163	28.2213
	44	4.4126	8.1111	0.7622	28.7519
	60	4.3058	8.799	0.788	28.3427
	74	4.2253	7.885	0.7869	29.402
	89	4.1944	8.1994	0.9701	27.9541
	104	4.0527	8.1344	0.8729	29.2741
	119	3.6864	8.6083	1.2073	28.3368
	134	3.6296	8.2236	1.0529	29.1138
	165	3.2295	8.838	0.9643	29.3396
	179	3.1506	8.1319	0.7521	29.7331
	193	3.0692	8.1319	0.6298	30.6107
	209	2.7768	8.5268	0.6152	30.0087
	225	2.8512	7.6583	0.5697	31.8591
	239	2.8159	7.902	0.316	30.9574
	254	2.761	8.124	0.4529	31.352
	269	2.7178	7.692	0.3797	31.9137
	285	2.6062	7.9182	0.4999	31.784
	330	2.5363	7.8207	0.2141	31.9705
	344	2.5112	7.6056	0.2608	32.0843
	359	2.4032	8.1547	0.3134	31.5142
	373	2.4978	7.9487	0.2717	32.6467
	390	2.5094	7.5606	0.2748	32.5701
	404	2.6388	7.5749	0.204	32.601
	418	2.5087	8.0032	0.2086	31.758
	434	2.5277	7.5583	0.2874	32.191
	478	2.6021	7.7261	0.2932	33.3957
	495	2.4432	7.4876	0.2213	32.6614
	510	2.4047	8.0255	0.2167	33.1448
	524	2.4125	7.6262	0.3523	32.9709
	538	2.4144	7.8239	0.3044	31.9804
	555	2.4395	7.676	0.265	32.1021
	569	2.4646	8.2338	0.3134	32.4073

Table A.4 (cont'd): Major Element Zoning for MVE12-66-4-002.1

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	583	2.4127	7.5157	0.2716	32.7935
	599	2.4316	7.3279	0.1887	33.3029
	614	2.3236	7.7776	0.3831	33.0805
	629	2.3488	7.884	0.2121	32.3958
	644	2.4142	7.9661	0.2591	32.698
	659	2.3364	7.6686	0.2783	33.6136
	674	2.3681	7.5937	0.2868	32.7296
	689	2.4899	7.2507	0.3312	32.9103
	703	2.3499	7.736	0.3816	33.0667
	720	2.3935	7.9969	0.3532	31.971
	734	2.4057	7.6692	0.358	32.285
	748	2.4716	7.8627	0.2807	32.2574
	780	2.3492	8.0837	0.422	33.1851
	794	2.2591	8.3669	0.4035	31.9645
	809	2.3225	8.1289	0.3409	31.9201
	839	2.2954	7.4126	0.3116	33.1846
	854	2.2918	7.6717	0.3689	32.7894
	868	2.3146	8.0179	0.3425	33.1372
	885	2.3593	7.5941	0.2536	32.2138
	899	2.139	7.7823	0.4095	32.018
	913	2.2755	8.1229	0.3176	32.7292
	929	2.1751	8.1948	0.4822	31.9197
	945	2.1809	8.0831	0.4878	31.9769
	959	2.2935	7.7503	0.4084	32.3643
	973	2.3718	7.5639	0.4997	32.6827
	989	2.3697	7.7449	0.4828	31.6207
	1005	2.4373	7.4292	0.5493	32.7581
	1019	2.1561	8.1439	0.5182	31.8966
	1033	2.2732	7.9995	0.5305	32.0027
	1050	2.2069	7.7211	0.5369	32.5684
	1065	2.2101	8.0699	0.4695	31.8004
	1079	2.2893	7.4464	0.4314	31.822
	1094	2.1643	7.9935	0.5226	31.9034
	1110	2.1792	8.3913	0.5852	31.6311
CORE	1124	2.1939	8.4809	0.533	31.7447

Table A.5: Major Element Zoning for MVE12-66-4-003.3

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.8638	8.4273	1.2536	27.0476
	16	4.0901	8.4671	0.9573	27.2279
	31	3.9524	8.8874	0.9332	26.9633
	46	3.931	9.0887	1.0374	27.0827
	61	3.4969	9.6528	1.4543	26.7348
	76	2.9296	9.3891	2.7289	25.803
	121	2.6008	9.5591	2.1704	27.2579
	135	2.6144	8.9644	1.7821	28.1248
	151	2.8733	9.135	2.4727	27.1292
	226	2.5827	7.9496	0.7442	30.2411
	241	2.3465	8.509	0.6413	30.3248
	271	2.407	8.5773	0.5563	31.7782
	286	2.2535	8.7041	0.5947	30.727
	301	2.8247	8.9268	0.7551	28.4576
	316	2.283	9.0431	0.7335	29.7789
	346	2.1671	8.1968	0.8043	30.208
	376	2.205	8.0991	1.1023	31.2571
	421	2.0761	8.1991	1.3935	29.865
	481	1.7224	8.8078	1.627	30.0916
	496	1.7692	8.4807	1.43	29.5743
	511	1.8982	7.9676	1.7008	30.9448
	541	1.7333	8.1416	1.6036	31.2452
	556	1.7051	8.692	1.7972	29.5051
	570	1.6407	8.1072	1.9436	31.0237
	587	1.6103	8.9516	1.9535	29.6125
	601	1.7055	8.5263	2.1049	31.0986
	616	1.6132	8.2619	1.9377	30.1674
	630	2.4892	8.4996	1.9478	28.166
	646	1.6613	8.2179	2.0216	29.6806
	676	1.5626	8.4173	2.6911	29.94
	706	1.5896	7.9315	2.8251	30.3273
	721	1.4564	8.7162	2.7484	30.4048
	736	1.5053	8.1036	2.8664	29.8318

Table A.5 (cont'd): Major Element Zoning for MVE12-66-4-003.3

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	751	1.3474	8.5292	2.8321	30.0386
	766	1.3983	8.9592	3.0344	29.3504
	781	1.3749	8.539	3.2294	29.465
	796	1.4257	8.2727	3.1641	30.079
	811	1.3904	8.8929	3.2082	30.3523
	826	1.2515	8.2819	3.3956	29.7558
	841	1.3956	8.3098	3.5508	29.4454
	856	1.285	8.4892	3.7105	29.3937
	871	1.3572	8.2908	3.5463	29.3229
	886	1.3577	8.6668	3.6504	29.1979
	916	1.3429	9.4983	3.4802	28.9732
	931	1.4569	7.9392	3.5869	30.0151
	946	1.3985	7.908	3.5636	29.7919
CORE	961	1.3306	8.5788	3.3982	27.9464

Table A.6: Major Element Zoning for MVE12-66-4-003.6

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.6479	7.7826	1.2544	27.3622
	16	3.8171	7.7852	1.1965	26.9249
	33	3.8057	7.843	1.1456	26.9444
	48	3.6498	8.0232	1.4896	27.4436
	63	3.0263	8.4122	2.6971	26.636
	78	2.5583	8.5278	2.647	26.9902
	93	2.2821	9.0722	2.2924	26.6201
	138	2.6682	8.4833	1.68	26.7738
	152	2.6364	7.9	1.369	28.1967
	174	2.28	7.6273	1.1151	29.7646
	204	2.3076	7.5372	0.8325	30.8717
	218	2.4315	7.5951	0.8209	29.3772
	249	2.155	7.4645	0.5156	30.9766
	263	2.2172	7.3038	0.7111	30.2387
	278	2.2684	7.3158	0.5559	30.2641
	309	2.0862	7.4559	0.7661	29.6344
	324	2.1175	7.6344	0.6504	30.5692
	339	2.1898	7.6888	0.7753	30.6224
	355	1.9998	7.823	0.9007	30.3137
	369	2.118	7.3788	1.0265	29.9397
	383	2.0032	7.482	0.9888	30.5225
	398	1.9477	7.0951	1.1271	30.3932
	413	1.8939	7.6457	1.3977	29.8579
	428	1.8248	7.6216	1.3849	30.3154
	442	1.9043	7.7237	1.4839	30.6263
	459	1.7249	7.5657	1.4482	30.4462
	482	1.8093	7.763	1.4478	30.511
	496	1.7491	7.5604	1.7644	30.265
	512	1.7694	7.7901	1.7903	29.9606
	527	1.7713	7.4907	1.7614	30.6217
	542	1.9623	7.9675	1.6211	28.0851
	556	1.8962	7.725	1.7178	29.5649
	587	1.8877	7.7929	1.937	28.4445
	601	1.5482	7.4007	2.1494	29.7398
	617	1.9019	7.9254	2.0687	28.6479

Table A.6 (cont'd): Major Element Zoning for MVE12-66-4-003.6

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	633	1.4994	7.3405	2.1089	29.786
	647	1.4864	7.7793	2.5054	29.5838
	661	1.6292	7.607	2.5906	28.6883
	706	1.3355	7.721	3.1334	29.6994
	721	1.3591	7.8535	3.3763	28.267
CORE	737	1.5311	7.4759	3.2947	29.7152

Table A.7: Major Element Zoning for MVE12-66-4-003.7

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.0751	9.3042	2.6184	26.8614
	75	2.4572	8.7464	1.7377	28.9197
	90	2.3677	9.0864	1.5263	28.9433
	105	2.4618	8.7652	1.6004	30.3773
	120	2.435	8.2054	1.3685	30.4847
	135	2.3107	8.5044	1.2844	30.9158
	150	2.2804	7.8088	0.9441	31.3895
	165	2.6248	8.5203	0.8599	29.3084
	180	2.2542	7.8828	0.9565	31.8224
	195	2.3808	8.2034	0.7272	31.4602
	225	2.272	8.1849	0.5858	32.2905
	240	2.3513	8.0342	0.6069	31.8324
	255	2.2952	8.1707	0.4597	31.8471
	270	2.3244	8.2852	0.6333	30.9101
	285	2.3116	8.4483	0.5703	31.6866
	300	2.1628	8.2336	0.6069	31.8524
	315	2.1989	8.6909	0.6961	31.6783
	330	2.2552	8.0865	0.6569	32.5474
	375	2.0572	8.6903	0.6369	31.1538
	390	2.2111	8.3828	0.716	32.2924
	420	2.2326	8.5355	0.7634	31.1301
	435	2.239	8.0804	0.9151	31.5118
	450	2.0797	8.0005	0.7652	32.3142
	465	2.2201	8.0277	0.8817	32.6987
	480	2.1294	8.1802	0.8971	31.4881
	495	2.132	8.4716	0.9479	31.4311
	510	2.0509	8.1435	1.0033	31.7282
	525	1.9857	7.9435	1.3036	31.8941
	540	1.9588	8.6562	1.1734	31.2172
	555	1.8773	8.53	1.4003	31.2818
	585	1.8735	8.3794	1.4422	30.534
	600	2.0936	8.7543	1.4534	30.4646
	615	1.7176	8.2335	1.4782	31.3972
	630	1.7779	8.3978	1.2223	30.7558
	645	1.9123	7.8306	1.3206	31.9967

Table A.7 (cont'd): Major Element Zoning for MVE12-66-4-003.7

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	660	1.8171	8.9121	1.3558	30.8611
	675	1.9275	8.5537	1.3665	30.7173
	690	1.9882	8.4571	1.2231	32.017
	704	2.1189	8.0193	1.2887	32.0675
CORE	720	2.0533	7.9876	1.1911	31.7734

Table A.8: Major Element Zoning for MVE12-66-4-003.9

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	3.7275	8.5086	1.2701	28.4708
	15	3.9611	8.4628	0.8747	27.915
	30	4.0162	8.6648	1.1944	28.4009
	45	3.955	8.324	1.0544	28.1732
	60	3.9035	8.8433	1.0512	28.5652
	75	4.2296	8.1813	0.9786	28.6233
	90	4.1738	8.5954	1.0262	28.2253
	105	3.9851	8.4898	1.1237	28.689
	120	3.2995	9.424	2.313	26.0156
	135	2.9059	9.7465	2.6867	27.2408
	150	2.571	9.2333	2.3982	27.6664
	165	2.4977	8.7984	2.2591	28.6861
	180	2.5175	8.7645	1.678	30.1057
	195	2.4411	8.8014	1.4865	29.7819
	210	2.2479	9.7957	1.2999	28.2497
	225	2.2647	8.7931	1.4074	30.5815
	240	2.5285	8.4065	1.1469	30.3709
	255	2.4063	8.272	1.1392	30.8893
	270	2.3469	8.2931	0.9285	31.7768
	285	2.3032	8.1805	0.707	31.729
	300	2.3252	7.9729	0.4682	32.015
	315	2.4002	7.78	0.4495	32.1099
	330	2.3215	8.4292	0.4295	31.247
	345	2.2888	7.8426	0.5209	31.8967
	360	2.3452	8.1094	0.5717	32.2961
	375	2.2938	8.0592	0.596	32.0636
	390	2.2636	7.9968	0.6064	31.8745
	404	2.1814	8.4515	0.6601	31.4811
	450	2.17	8.2779	0.8964	32.2747
	480	2.168	8.1919	0.9309	32.1946
	495	2.042	8.4209	0.8224	31.4879
	510	2.0452	8.4307	0.9854	31.5239
	525	1.9912	8.3502	1.1443	31.415
	540	1.889	8.3127	1.4234	31.0899
	555	1.6918	8.4548	1.4252	31.4096

Table A.8 (cont'd): Major Element Zoning for MVE12-66-4-003.9

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	585	1.886	8.2704	1.5245	30.837
	600	1.7026	8.3938	1.6885	31.3686
	615	1.7468	8.3685	1.7008	31.6982
	629	1.559	8.4745	1.6852	31.562
	645	1.7366	8.2486	1.701	30.3892
	660	1.6518	8.743	1.8221	31.0254
	675	1.7467	8.5931	1.7359	31.155
	690	2.255	8.8967	1.6152	30.0898
	705	1.6119	8.3166	1.8515	31.0806
	720	1.7537	8.2153	1.8098	32.1683
	735	1.7379	8.4953	1.6496	30.8856
	750	1.6896	9.1183	1.7534	30.6898
	765	1.689	8.7577	1.7941	30.6957
	780	1.9868	8.5355	1.902	30.5749
	795	1.6238	8.4356	1.932	30.99
	810	1.6144	8.2902	1.801	30.9384
	825	1.6025	8.2927	1.9831	30.5123
	930	1.6784	8.8097	1.8003	31.1684
	945	2.3067	8.5458	1.8303	31.561
	960	1.6552	8.8628	1.7427	30.0779
	975	1.7448	8.008	1.8515	31.19
	990	1.6807	8.2798	1.5698	31.5009
	1005	1.7227	8.4618	1.7115	31.5956
	1020	1.5971	8.8974	1.8953	30.2554
	1035	1.7242	8.5769	1.746	31.4425
	1050	1.7825	8.661	1.8723	31.4308
	1065	1.7148	8.4253	1.5806	31.2599
	1080	1.8132	8.17	1.3964	31.4106
CORE	1095	1.7275	8.428	1.6981	30.7862

Table A.9: Major Element Zoning for MVE12-66-7.1

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	1.404	9.0893	2.2145	30.5716
	18	1.6482	8.6933	1.667	30.1234
	64	1.821	8.9621	1.6041	29.8866
	78	2.2026	8.3393	1.4849	31.3026
	92	2.7015	8.0077	1.0566	30.9139
	138	2.7219	7.718	0.3665	32.5975
	152	2.6028	7.2648	0.2883	33.7107
	169	2.1815	7.3975	0.4487	33.4559
	183	2.138	7.8248	0.3942	33.2374
	198	2.1579	7.6079	0.259	33.3082
	214	2.3249	7.8952	0.199	33.1406
	226	2.1306	7.574	0.2017	33.336
	240	2.0024	8.3407	0.0422	32.2283
	254	2.041	8.0802	0.3006	33.5351
	268	2.0024	7.4744	0.2855	33.1215
	292	1.7348	7.9215	0.3317	33.5072
	308	1.7451	7.4829	0.2683	34.491
	321	1.5825	8.2219	0.3336	33.8069
	342	1.7101	7.7244	0.4325	33.4096
	357	1.5329	7.8207	0.3093	33.669
	371	1.5391	8.0854	0.3595	33.9668
	384	1.4297	8.4271	0.3136	32.8348
	399	1.5697	7.8309	0.3424	33.9486
	414	1.4553	9.2532	0.3229	32.6927
	489	1.4411	8.9835	0.3746	32.782
	505	1.4001	8.2376	0.3189	33.3537
	519	1.6354	8.0575	0.2275	33.486
	534	1.302	8.2564	0.3469	33.8819
	549	1.3286	7.9544	0.4009	34.4516
	564	1.2849	8.3537	0.2541	33.8085
	579	1.3566	8.2538	0.288	33.2797
	593	1.3217	8.2946	0.3012	32.7882
	610	1.3102	8.0961	0.3893	33.4939
	627	1.3492	8.3024	0.2964	33.7591
	642	1.376	8.071	0.2446	34.1319

Table A.9 (cont'd): Major Element Zoning for MVE12-66-7.1

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	653	1.337	7.6811	0.2965	34.085
	659	1.2584	8.7184	0.3389	33.3519
	689	1.3536	7.8296	0.2626	33.9319
	703	1.3619	7.7167	0.3723	33.9397
	717	1.227	8.3264	0.3371	33.4966
	732	1.3027	8.1398	0.3227	33.8747
	747	1.3185	8.1381	0.3441	33.5738
	761	1.3065	8.5438	0.2548	33.979
	778	1.2838	8.5891	0.2026	32.9862
	792	1.2823	8.2576	0.4491	33.1745
	822	1.312	7.8251	0.3257	33.836
	838	1.2986	8.6855	0.2533	33.3484
	852	1.376	8.4753	0.3667	33.2784
	866	1.3263	8.2159	0.3281	34.1072
	882	1.2391	8.5043	0.228	33.1929
	897	1.287	7.8947	0.2756	34.7399
	912	1.4197	7.8423	0.3722	33.9128
	926	1.4897	7.8503	0.2816	34.2751
	956	1.3089	8.3047	0.3525	33.4166
	970	1.4722	7.3993	0.3804	33.9617
	983	1.4665	7.5213	0.3138	34.1022
	989	1.433	8.1745	0.3526	33.6861
	1050	1.6041	7.8778	0.3047	33.6631
	1065	1.7901	6.7707	0.3993	34.8082
	1111	1.6865	7.4731	0.3719	33.1987
	1125	1.5979	7.8173	0.3198	33.232
	1140	1.5343	7.9362	0.3836	33.5621
	1155	1.674	7.2496	0.2093	33.8253
	1171	1.7515	7.3332	0.4345	33.3864
	1185	1.5031	7.654	0.3124	33.6555
	1199	1.5876	7.5864	0.4439	33.7167
	1215	1.6597	7.3567	0.3477	33.1319
CORE	1230	1.635	7.6567	0.3614	34.0537

Table A.10: Major Element Zoning for MVE12-66-7.3

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	14	1.3918	9.6196	2.0769	28.9919
	30	1.4144	9.5089	2.1301	30.0977
	45	1.5088	9.1251	1.6179	29.7057
	60	1.7198	8.2612	1.5717	28.576
	76	1.8647	8.979	1.4545	29.2263
	81	1.8991	8.9694	1.1292	29.6415
	96	1.7968	8.4902	1.3344	30.2197
	111	1.7195	8.66	2.2155	29.9503
	125	2.2694	8.1553	1.398	29.6896
	139	2.2333	7.7901	1.5821	29.3718
	155	2.7533	7.5476	1.4332	30.0298
	169	2.8914	7.3082	0.7758	30.3155
	183	2.7993	7.5399	0.561	30.4935
	200	2.8649	7.5096	0.458	31.1367
	215	2.9186	7.758	0.3341	29.831
	229	2.7176	7.5723	0.3952	29.7938
	259	2.6241	7.5391	0.3127	30.7825
	274	2.337	7.3625	0.4636	31.1934
	288	2.197	7.5901	0.5173	31.8914
	304	2.3084	7.3456	0.5882	32.0376
	319	2.1792	7.686	0.3638	31.2048
	334	2.2325	7.6361	0.2735	31.059
	348	2.3234	7.8577	0.274	31.6617
	364	2.385	7.3222	0.229	31.5221
	379	2.4391	7.75	0.234	32.3412
	394	2.1989	7.3587	0.2011	31.7396
	407	2.2242	7.501	0.2336	32.2291
	413	2.2862	8.0087	0.2022	30.4748
	428	2.3515	7.1828	0.2318	28.5677
	457	2.0983	8.0462	0.2237	30.995
	472	2.0596	7.4675	0.2373	31.5357
	487	2.0985	7.3747	0.228	31.8099
	502	1.9856	8.8671	0.1747	30.3562

Table A.10 (cont'd): Major Element Zoning for MVE12-66-7.3

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	516	2.1951	7.6455	0.1959	31.5388
	529	2.1446	7.6102	0.2266	32.4381
	545	2.0078	7.4471	0.2479	32.4515
	559	1.9057	7.6339	0.2713	32.1558
	573	1.7041	7.7383	0.3616	31.8774
	589	1.7339	7.836	0.2949	33.1443
	619	1.6523	7.6171	0.3535	33.3435
	678	1.5655	7.6501	0.3903	31.7119
	694	1.7953	7.9628	0.3934	30.7721
	710	1.4418	9.0296	0.3327	30.606
	724	1.5648	7.6777	0.3092	32.8608
	738	1.4359	8.1916	0.3045	31.8936
	754	1.3905	8.9676	0.2786	31.8322
	769	1.5779	7.3933	0.3557	32.291
	784	1.44	8.2704	0.3004	31.6996
	815	1.4372	8.2867	0.3277	31.2266
	829	1.5516	8.1781	0.2713	31.3196
	859	1.5357	7.3771	0.3051	30.6797
	874	1.7084	7.3643	0.3377	27.9775
	889	1.4544	7.8929	0.4008	32.2493
	903	1.4306	7.7231	0.411	32.8992
	919	1.4855	7.7588	0.3763	32.785
	935	1.6833	7.4182	0.3732	31.9147
	949	1.8686	8.4242	0.4072	29.8584
	980	1.286	8.4448	0.3991	31.1768
	994	1.3844	7.8779	0.306	32.025
	1008	1.399	8.08	0.2769	31.8649
	1024	1.5049	7.7344	0.1381	32.2436
	1034	1.3298	7.6153	0.3109	32.9634
CORE	1048	1.42	7.8255	0.3195	32.6013

Table A.11: Major Element Zoning for MVE12-66-7.4

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	1.8105	7.6574	1.6992	30.08
	15	1.9007	7.392	1.6605	30.5883
	30	2.4277	6.968	1.5032	30.305
	45	3.0495	7.0851	0.5063	30.5394
	60	3.1336	7.1491	0.452	31.1168
	90	2.8873	6.9486	0.5279	31.0751
	105	2.7121	6.9412	0.3366	31.9561
	120	2.4092	7.0126	0.2931	32.042
	135	2.2908	7.03	0.3987	32.9721
	150	2.1664	7.1799	0.4953	32.4237
	195	2.4178	6.7661	0.2914	31.8783
	240	2.0573	7.0709	0.2313	32.6831
	255	1.8255	7.0205	0.352	32.4796
	270	1.8994	7.0234	0.3562	33.1725
	285	1.819	7.122	0.2737	33.1912
	300	1.7344	7.2686	0.3566	33.0407
	315	1.6618	7.1278	0.3571	31.5054
	330	1.6724	6.9543	0.3357	32.5245
	345	1.6392	7.302	0.3909	32.4169
	360	1.6586	7.3906	0.2912	32.6324
	375	1.7695	6.828	0.2261	33.1769
	390	1.7177	7.1126	0.3774	32.627
	435	1.5782	7.0756	0.2292	32.6703
	450	1.6266	7.0413	0.3846	32.1598
	465	1.5179	7.7576	0.3247	32.0202
	480	1.5862	7.023	0.3145	33.3625
	495	1.6668	7.2439	0.2811	32.8265
	540	1.5637	7.2474	0.3874	33.0595
	555	1.682	6.7155	0.3733	32.7434
	570	1.6756	6.8919	0.2558	32.3654
	600	1.6537	6.9543	0.2066	33.1134
	630	1.4852	7.4653	0.2486	33.225
	690	1.4574	7.342	0.3091	33.5201
	705	1.4493	7.0767	0.3582	33.9623
	720	1.5089	6.6776	0.4018	33.8324

Table A.11 (cont'd): Major Element Zoning for MVE12-66-7.4

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	735	1.4346	6.8647	0.3555	33.4429
	750	1.4526	7.1418	0.2941	32.8703
	765	1.584	7.2296	0.1988	32.6438
	795	1.394	6.7603	0.3629	33.8182
	810	1.4975	6.9691	0.4058	33.4738
	825	1.4388	7.1597	0.2804	33.2047
	840	1.3152	7.5711	0.2834	33.0892
	855	1.4236	7.6305	0.2218	32.5976
	870	1.3815	7.2476	0.335	32.8995
	900	1.3706	6.9448	0.2595	33.3081
	915	1.3447	7.2802	0.3664	33.7762
	945	1.4396	7.2069	0.2505	33.4973
	960	1.2409	7.6011	0.2507	33.7412
	1005	1.2451	7.8501	0.2191	32.7942
	1019	1.2887	7.9627	0.2525	32.8984
	1064	1.4193	7.038	0.179	33.7251
	1079	1.3283	7.4901	0.2405	32.2384
	1094	1.2637	7.5998	0.3047	32.0383
	1109	1.157	7.9649	0.2505	32.2999
	1126	1.3744	7.1594	0.3517	33.1238
	1171	1.2808	7.4464	0.2372	33.2806
	1186	1.2529	7.4404	0.2054	33.4721
	1201	1.2469	7.6401	0.3016	33.1732
	1216	1.1898	7.5608	0.2577	32.5018
	1231	1.2641	7.3219	0.2858	33.619
	1246	1.3331	7.2468	0.1864	32.9035
	1261	1.1931	7.5646	0.1764	32.9379
	1276	1.2344	7.5614	0.2492	33.2555
	1291	1.2159	7.3959	0.2197	33.5783
	1306	1.1849	7.4493	0.2634	32.1458
	1321	1.2534	7.248	0.2429	33.137
	1336	1.154	7.5506	0.2182	33.2735
	1366	1.2524	7.553	0.3664	32.3576
	1381	1.2842	7.2372	0.3184	32.5006
CORE	1396	1.1805	7.3697	0.2507	32.7313

Table A.12: Major Element Zoning for MVE12-66-7.5

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
RIM	0	1.2294	9.9794	2.4963	29.2735
	15	1.7631	8.695	1.4008	30.3169
	30	2.0059	8.7617	1.4529	31.2602
	45	2.5206	7.9592	1.1287	31.5524
	60	2.8782	7.6647	0.9442	31.0634
	75	2.9658	7.331	0.7673	31.7888
	120	2.6487	7.6039	0.3714	31.8424
	135	2.5692	7.7626	0.2405	32.5646
	150	2.149	7.5934	0.4958	33.3492
	165	2.1239	7.5322	0.4488	32.7322
	180	2.1116	7.8763	0.4052	32.5451
	195	2.2143	7.5015	0.4004	32.9101
	210	2.2606	7.3035	0.1652	32.7788
	240	1.8932	7.8364	0.2578	33.813
	255	1.8087	7.494	0.2299	34.1085
	270	1.805	7.6735	0.3518	33.8588
	284	1.6886	7.2955	0.3718	35.6385
	300	1.6542	8.1017	0.2612	33.347
	315	1.5748	7.9191	0.1944	33.5256
	330	1.4801	8.2681	0.4063	34.3103
	345	1.492	8.3231	0.3537	32.3779
	360	1.6065	7.8645	0.3419	33.9433
	375	1.3793	8.9966	0.3014	33.12
	390	1.4469	8.7151	0.3119	32.5999
	405	1.4297	8.1563	0.1947	32.7619
	420	1.4037	9.1913	0.2864	32.9448
	435	1.3223	9.4381	0.3471	32.44
	450	1.3597	7.4111	0.2849	32.8109
	465	1.3509	8.0766	0.3066	34.0344
	480	1.3662	7.4956	0.3633	34.034
	495	1.4358	7.8685	0.3911	33.4997
	510	1.4021	8.15	0.327	33.0265
	570	1.3218	8.7183	0.2419	33.5353
	585	1.3293	7.3964	0.2697	34.1569
	600	1.2822	8.4932	0.2956	33.4138

Table A.12 (cont'd): Major Element Zoning for MVE12-66-7.5

		WT % OXIDE			
DISTANCE (μm)		MgO	CaO	MnO	FeO
	615	1.2246	8.5675	0.1878	33.9193
	645	1.3385	7.8168	0.2767	34.2729
	660	1.2234	8.2405	0.3556	34.0729
	675	1.2692	8.4378	0.3473	33.41
	690	1.2622	7.8265	0.2496	34.2294
	705	1.2401	8.1193	0.2033	34.0017
	720	1.1542	9.3515	0.2568	32.552
	735	1.0882	10.2432	0.3312	31.8236
	750	1.0324	10.2585	0.1704	31.7329
	765	1.1296	8.8786	0.3209	33.029
	780	1.1477	8.6828	0.1828	33.8884
	795	1.1657	7.7139	0.3073	34.6537
	810	1.1761	8.4872	0.1831	34.0236
	825	1.1842	8.3394	0.2585	33.4301
	840	1.1723	7.7389	0.3203	33.9091
	855	1.0748	8.9407	0.3121	32.9237
	915	1.1413	8.9341	0.2666	33.3967
	930	1.1824	7.221	0.3274	34.7943
	945	0.9646	9.8591	0.3554	32.0449
	960	1.0786	9.461	0.4255	33.6622
	975	1.0102	9.2305	0.2545	33.161
	1050	1.0589	8.6648	0.5285	33.673
	1065	0.9637	10.2282	0.4672	31.7199
	1080	0.9137	10.4609	0.603	31.5136
	1095	0.8809	10.4566	0.5796	31.3796
	1110	0.914	10.3297	0.6509	32.4968
	1125	0.8777	10.1875	0.5412	32.0263
	1140	0.9486	9.4461	0.5208	32.589
	1155	0.9481	9.3405	0.5375	32.2864
	1200	0.9506	9.4993	0.6344	32.9735
	1215	0.9515	9.4347	0.5971	32.9355
	1230	0.8973	9.2359	0.5466	32.3477
	1245	0.9321	8.2305	0.7624	34.0647
CORE	1260	1.0242	8.041	0.5833	33.1063