

TECTONIC EVOLUTION OF THE BAIE VERTE MARGIN, NEWFOUNDLAND

by

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This thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Statement of Contributions

Thesis Chapters 1 and 5 were authored solely by Ludovico Scorsolini, with input and guidance from the thesis supervisors, Chris Yakymchuk and Cees van Staal. Chapters 2–4 are manuscripts prepared for submission to academic journals, with Ludovico Scorsolini as the primary author responsible for writing, data interpretation, and figure preparation. Ludovico Scorsolini also collected all samples, and, where feasible, conducted sample preparation and analyses. The specific contributions of co-authors and collaborators for each chapter are detailed below:

Chapter 2 was submitted to the *Journal of Metamorphic Geology*. Ludovico Scorsolini was responsible for the majority of the manuscript, including writing, figure preparation, modeling, and compiling data from existing literature. Sample crushing, mineral separation, and mineral picking were performed by Ludovico Scorsolini, with assistance from John Hanchar (committee member) and Matt Crocker at Memorial University of Newfoundland. John Hanchar prepared the grain epoxy mounts. Whole-rock lithogeochemical analysis was conducted at Actlabs (Ontario). Thin section preparation was done by VanPetro (Vancouver) and Ludovico Scorsolini. Chris Yakymchuk (supervisor) provided guidance on the text, modeling results, and figures, while Cees van Staal (supervisor) helped refine the text and articulate the tectonic implications. John Hanchar advised on analytical methods and contributed comments on the text. Ludovico Scorsolini performed laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) analysis and electron microprobe analysis, with assistance from John Hanchar, Wanda Aylward, Markus Walle, and Sebastian

Kommeshier at Memorial University of Newfoundland, who also performed preliminary data processing (applicable to Chapters 2, 3, and 4). Sebastien Dyer (co-author) assisted with the development and implementation of thermodynamic models using Theriak-Domino.

Chapter 3 is planned for submission to the *Geological Society of America Bulletin* in 2024. Ludovico Scorsolini wrote the manuscript, created the figures, conducted LA-ICP-MS and electron microprobe analyses, processed and interpreted the data. He also prepared the samples and mounted the grains in epoxy. John Hancher (committee member) and Nina Heinig carried out cathodoluminescence imaging of zircon. Chris Yakymchuk and Cees van Staal provided guidance and feedback on the text, with Chris Yakymchuk also offering advice on interpreting the geochronological results.

Chapter 4 will be submitted to *Tectonics* in 2024. Ludovico Scorsolini was primarily responsible for the manuscript, including writing, figure preparation, field data collection, and interpretation. The co-authors—Cees van Staal, Chris Yakymchuk, and John Hancher—provided comments on the text and figures. Additionally, Cees van Staal (supervisor) offered guidance on data interpretation.

Abstract

Located along the Early Paleozoic Laurentian continental margin in Newfoundland, the Baie Verte Margin tectonostratigraphy and tectono-metamorphic evolution have been controversial for decades. Here, the results of a detailed field, petrological and geochronological study are presented, where Baie Verte Margin is subdivided into three tectono-metamorphic units separated by tectonic contacts: the East Pond Metamorphic Suite (EPMS) basement, EPMS cover, and the Fleur de Lys Supergroup (FdLS). Each unit exhibits a distinct metamorphic and structural evolution recorded during the subduction, exhumation, and post-collisional history of this ancient margin. The combination of thermodynamic modelling, petrochronology, and structural analysis provided insights into the P-T-t-d paths of the studied units, allowing a better understanding of their role during the evolution of the Taconic subduction system. High-pressure (HP) to ultra-high-pressure (UHP) conditions were reached between 483 and 475 Ma during the D1 phase, with the EPMS cover recording eclogite-facies metamorphism at ~2.8 GPa and 620°C. Subsequent decompression resulted in a β -shaped pressure-temperature-time (P-T-t) path, with near-isothermal decompression to ~2 GPa and heating to 860°C during exhumation. A multi-stage exhumation model is proposed for the EPMS eclogites: 1) buoyant rise through a low-density mantle wedge and 2) subsequent ascent at shallower crustal levels, facilitated by external tectonic forces and slab break-off, as evidenced by Late Taconic magmatism.

While the EPMS cover re-equilibrated at UHP conditions, the EPMS basement and FdLS experienced decompression and Barrovian metamorphism during late-D1, indicating

decoupling of the units during this stage. Coupling between the units occurred along a D2 shear zone during retrograde metamorphism, spanning 475–452 Ma.

Two exhumation scenarios are proposed to explain the tectonic evolution of the margin: (i) Following late D1 detachment, the EPMS basement and FdLS were exhumed to crustal levels while the EPMS cover was subducted deeper into the mantle. Tectonic extrusion along D2 shear zones, potentially aided by melt weakening, then emplaced the EPMS cover between the two units. (ii) Alternatively, sequential detachment occurred from the top to the bottom of the slab, resulting in deeper subduction of lower units, followed by their exhumation through back-folding and crustal wedge thrusting.

The Silurian F3 folding deforms both D1-2 structures in each unit and the D2 shear zones that bound them, suggesting that the continental wedges, which recorded different tectono-metamorphic paths after early D1, were juxtaposed before the onset of deformation associated with the Salinic Orogeny. Later deformation phases, D4 and D5, are probably related to tectono-metamorphic activity related to the Acadian and Neo-Acadian orogenies.

This research improves our understanding of the dynamic tectono-metamorphic evolution of the Baie Verte Margin, emphasizing the role of fluids, thermal perturbations, and deformation in driving metamorphic reactions, and exhumation. The findings contribute to understanding the mechanisms controlling HP-UHP terrain evolution in subduction zones and highlight the complex interactions between subduction, exhumation, collision, and magmatism throughout the Taconic orogeny.

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Table of Contents

Author's Declaration	iii
Statement of Contributions.....	iv
Abstract.....	vi
Acknowledgments	viii
List of Figures.....	xiii
List of Tables	xv
Chapter 1: Introduction	1
1.1 Introduction	1
1.2 The Canadian Appalachians	2
1.3 Tectonic Evolution of the Canadian Appalachians.....	3
1.4 Taconic Orogeny in Northern Newfoundland	5
1.5 Eclogite and Amphibolite of the Baie Verte Margin.....	7
1.6 Objectives	9
1.6 Thesis Organization	10
1.7 Publication of Chapters	11
Chapter 2: Exhumation mechanisms of high-pressure rocks with high-temperature overprinting: insights from eclogites of the Baie Verte Peninsula, Newfoundland	16
Summary:.....	16
2.1 Introduction	17
2.2 Regional Geology.....	19
2.3 Eclogite and Amphibolite of the Baie Verte Peninsula.....	22
2.4 Methods.....	23
2.4.1 Sampling.....	23
2.4.2 Electron Microprobe Analysis.....	23
2.4.3 LA-ICPMS trace elements analysis of rutile	24
2.4.4 Whole-Rock Compositions.....	25
2.4.5 Phase Equilibria Modelling	25
2.4.6 Zr-in-Rutile Thermometry	27
2.5 Field Relationships	28
2.6 Mineral Assemblages and Microstructures	29
2.6.1 Preserved Eclogites.....	29
2.6.2 Katophorite-bearing Partially Retrogressed Eclogites	30
2.6.3 Pargasite-bearing Completely Retrogressed Eclogites.....	32
2.7 Mineral Compositions.....	33

2.7.1 Amphibole	33
2.7.2 Omphacite.....	34
2.7.3 Garnet	35
2.7.4 Phengite	35
2.8 Results of Phase Equilibria Modeling	35
2.8.1 Si-in-Phengite Barometry	38
2.8.2 Zr-in-Rutile Thermometry	38
2.9 P–T Evolution	39
2.10 Discussion	40
2.10.1 Limitations and Assumptions of Phase Equilibria Modelling.....	40
2.10.2 P–T–t path.....	43
2.10.3 Hydration During Exhumation	45
2.10.4 Heat and Fluids: Implications for Eclogite Exhumation Mechanisms	46
2.10.5 Tectonic Evolution and Global Correlations	49
2.11 Conclusions	51
Chapter 3: Petrochronology of the East Pond Metamorphic Suite, Baie Verte Peninsula, Newfoundland	64
3.1 Introduction	65
3.2 Regional Geology	66
3.3 Tectonometamorphic Evolution and Previous Geochronology	68
3.4 Petrography and Accessory Mineral Imaging.....	72
3.5 Mineral Compositions.....	72
3.6 U-Pb and Trace Element Petrochronology	73
3.6.1 Zircon U-Pb Analyses	73
3.6.2 Rutile U-Pb Analyses	73
3.6.3 Titanite Analyses	74
3.6.4 Apatite Analysis	74
3.6.5 Trace Element Analysis.....	74
3.7 Field Relationships	75
3.8 Sample Descriptions.....	76
3.9 Petrochronology	77
3.9.1 Zircon.....	77
3.9.2 Rutile	79
3.9.3 Titanite.....	80
3.9.4 Apatite	81
3.10 Discussion	82
3.10.1 Limitations and Assumptions	82
3.10.2 Tectonic Implications of the Petrochronological Record	84
3.10.4 Summary of the Taconic P–T–t Evolution.....	88
3.10.5 Late Taconic Magmatism and Implications for Exhumation of the EPMS	89

3.10.6 Tectonic Evolution of The Baie Verte Margin and The Notre Dame Arc During the Taconic Orogeny	90
3.11 Conclusions	91
Chapter 4: Tectono-metamorphic evolution of the Baie Verte Margin, Newfoundland	
.....	102
Summary	102
4.1 Introduction	103
4.2 Geological Setting	104
4.2.1 Overview of The Existing Tectono-Metamorphic Framework of The Baie Verte Peninsula.....	105
4.3 Methods	107
4.4 Results	108
4.4.1 Tectono-metamorphic Units of the Baie Verte Margin.....	108
4.4.2 Regional Structure of the Baie Verte Margin	111
4.4.3 Generations of Structures and their Relationships to Growth of Metamorphic Minerals	113
4.5 Discussion	116
4.5.1 Tectono-Stratigraphy and Regional Structure	116
4.5.2 Tectono-Metamorphic Evolution	117
4.5.3 Tectonic Model.....	120
4.6 Conclusions	125
Chapter 5: Summary and Conclusions	137
5.1 Main Conclusions	137
5.1.2 Tectono-Stratigraphy and Regional Structure of the Baie Verte Margin (Chapter 4)	137
5.1.3 Tectono-Metamorphic Evolution (Chapters 2 and 3).....	137
5.1.4 Subduction and Exhumation of the EPMS Eclogites (Chapter 2).....	138
5.1.5 Tectonic Model and Implications for Exhumation Mechanisms (Chapter 4)	139
5.2 Future Directions	140
References	142
Appendices	180
Appendix A1: Analytical Methods	180
Appendix A2: Samples Location	183
Appendix A3: Whole Rock Geochemistry	184
Appendix A4: Mineral Chemistry	185
Appendix A5: LA-ICPMS Trace Elements and U-Pb analysis	198

List of Figures

Figure 1.1: Geologic map of the northern portion of the Appalachians	12
Figure 1.2: Middle Cambrian–Middle Ordovician tectonic evolution of the peri-Laurentian realm	14
Figure 1.3: Regional geological map of Baie Verte Peninsula.....	15
Figure 2.1: Geological Map of the Appalachian-Caledonian orogenic belt	52
Figure 2.2: Eclogite boudin hosted in EPMS metasediments.....	53
Figure 2.3: Microphotographs of eclogite showing an increasing degree of retrogression	55
Figure 2.4: Compositions of amphiboles, pyroxenes, and phengite	57
Figure 2.5: Garnet EPMA WDS X-Ray maps and garnet EPMA traverses.....	58
Figure 2.6: P–M(H ₂ O) pseudosections at 700, 650 and 600 °C with amphibole isopleths	59
Figure 2.7: P–T pseudosection calculated for a sample of preserved eclogite	61
Figure 2.8: P–T diagram summarizing peak pressure and decompression history of East Pond Metamorphic Suite eclogites	62
Figure 3.1: Geological map of the Baie Verte Peninsula	93
Figure 3.2: Field photograph of the eclogite boudin margin, crosscutting pegmatite, and migmatite	94
Figure 3.3: Microphotographs of eclogite samples	96
Figure 3.4: Zircon CL images, Wetherill and Tera-Wasserburg concordia diagrams, weighted mean plot, and kernel density estimation diagrams	97
Figure 3.5: (Sm/La) _N vs. La diagram for zircon in pegmatite	98
Figure 3.6: Chondrite normalized REE profile plots.....	99
Figure 3.7: Box plot summarizing Zr-in-rutile and Zr-in-titanite thermometry data	100
Figure 3.8: Compilation of geochronology data of the Baie Verte Margin.....	101
Figure 4.1: Structural map of the Baie Verte Margin	127
Figure 4.2: Field and microphotographs of eclogite and metasediments of the East Pond Metamorphic Suite	129

Figure 4.3: Field and microphotographs of mafic boudins and metasediments of the Fleur de Lys Supergroup.....	131
Figure 4.4: Field photographs showing the major tectonic boundaries	133
Figure 4.5: Stereonets displaying structural measurements from different structural domains.	134
Figure 4.6: Schematic tectonic evolution of the Baie Verte margin.....	135

List of Tables

Table A1 - I: Summarized methods for EPMA and LA-ICPMS analysis.....	180
Table A2- I: GPS coordinates of the analyzed samples.....	183
Table A3 – I: Eclogites whole rock geochemistry.....	184
Table A3 – II: Whole rock compositions used for thermodynamic modelling	184
Table A4 – I: Representative compositions of the main amphibole generations	185
Table A4 – II: Representative compositions of garnet zones in sample 93LS1a	186
Table A4 – III: Amphibole chemistry.	187
Table A4 – IV: Clinopyroxene chemistry.....	189
Table A4 – V: White mica chemistry..	190
Table A4 – VI: Garnet chemistry..	191
Table A4 – VII: Rutile chemistry... ..	193
Table A4 – VIII: Titanite Chemistry.....	196
Table A4 – IX: Apatite Chemistry.....	197
Table A5 – I: Rutile trace elements and U-Pb analysis	198
Table A5 – II: Titanite trace elements and U-Pb analysis.....	205
Table A5 – III: Apatite trace elements and U-Pb analysis	208
Table A5 – IV: Zircon trace elements and U-Pb analysis.	211

Chapter 1: Introduction

1.1 Introduction

Taconic eclogites in northern Newfoundland are hosted in geologic units situated along the eastern edge of the Baie Verte margin, which is delineated by the suture zone of the Taconic orogen, the Baie Verte-Brompton Line (Fig 1.3) (de Wit, 1980; Hibbard, 1983; van Staal and Barr, 2012). They are exposed in Mesoproterozoic basement rocks (e.g. East Pond Metamorphic Suite), as mafic layers, pods, or lenses that crosscut the structures of their host rocks. These eclogites are interpreted as evidence that the hyperextended Laurentian margin was subducted to deep crustal levels during the Taconic orogenic cycle (495-461 Ma) (Castonguay et. al., 2014). Although the area has been extensively investigated since the second half of the last century (e.g. Williams 1964; de Wit 1980), there is still considerable debate about the structural relationships between the eclogitic mafic bodies and their host rocks. Additionally, preliminary thermobarometry suggested that the mafic pods were subjected to higher pressures than their hosts, and the reasons for this are unclear. Finally, the variability of the radiometric ages does not permit an univocal interpretation of the exhumation mechanisms of the subducted Baie Verte margin units (de Wit and Armstrong, 2015). The importance of these eclogites for understanding the Taconic orogeny and hence, the initial stages of the closure of the Iapetus Ocean (and related seaways) justifies a more detailed structural, petrological, and geochronological analysis. The goal of this project is to define the tectonometamorphic evolution as well as the timing and the exhumation mechanism of the Taconic eclogites. This objective is pursued by detailed structural analysis at outcrop to regional scales, combined with assembling a robust petrographic and geochronological dataset,

which contain petrologic and tectonic models for the development of the Taconic orogenic cycle and, thus, for the Cambrian-Ordovician evolution of the Laurentian realm in the northern Appalachians.

1.2 The Canadian Appalachians

The Canadian Appalachians represent the northern termination of the Appalachian–Caledonian mountain belt in North America, one of the Earth’s most studied orogens (Fig. 1.1). This long and narrow mountain belt was formed mainly by the Cambrian (515 Ma) through Permian (275 Ma) closure of the Iapetus and Rheic oceans and related seaways (van Staal and Barr 2012, and references therein). The sequence of oceanic closures eventually led to the Late Paleozoic Alleghanian collision, which culminated with the formation of the supercontinent Pangea (Hibbard et al. 2010; Nance et al. 2008; van Staal et al. 1998, 2009; Wilson 1966).

The Canadian segment of the Appalachian chain (Fig. 1.1) includes a complex tectonic collage of oceanic suprasubduction zones and microcontinental terranes, which were accreted to Laurentia throughout its Paleozoic evolution. During this period, the Laurentian margin of the Appalachians progressively expanded oceanwards due to the docking of terranes that had either Laurentian or Gondwanan provenance (van Staal et al. 2009a).

The evidence for early accretion-related orogenesis is especially well preserved in the Canadian Appalachians. This is because the Canadian segment of the orogen is located in the hinterland of the Alleghanian collision, therefore, it escaped the penetrative effects of this late-stage collisional event.

The Canadian Appalachians were historically divided into tectonostratigraphic zones and subzones (from west to east: Humber, Dunnage, Gander, Avalon, and Meguma) (Williams 1995; Williams 1979; Williams et al. 1988), separated by major faults. Hibbard et al. (2007) and van

Staal and Barr (2012) revised the former zonal terminology in light of the then most recent observations. Williams' (1979) Humber Zone represents the Cambrian-Ordovician Appalachian margin of Laurentia, now referred to as the Humber margin where it faced an open ocean, and the Baie Verte margin where it faced the Dashwoods microcontinent.

The former Gander, Avalon, and Meguma zones are interpreted to be the vestiges of three distinct Gondwana-derived microcontinents and are now referred to as Ganderia, Avalonia, and Meguma, respectively (Fig.1.1). The Dunnage Zone outcrops between the Humber and Gander zones, comprises fragments of continental and oceanic arc terranes that were present in the Iapetus Ocean prior to their accretion to Laurentia. During this episodic accretionary evolution, the Laurentian margin expanded oceanwards, into what is now called composite Laurentia (van Staal and Barr, 2012).

1.3 Tectonic Evolution of the Canadian Appalachians

The accretion of the continental and oceanic terranes that occurred during the Paleozoic was episodic, and different tectonic cycles are now identified within the Canadian Appalachian: the Taconic, Penobscot, Salinic, Acadian, Neoacadian, and Alleghanian orogenic cycles.

The Taconic orogenic cycle took place between the Late Cambrian and Late Ordovician (ca. 500–450 Ma). It is divided into three different stages that encompass subduction and accretion of oceanic and continental arcs in the peri-Laurentian realm (van Staal et al., 2007) (Fig. 1.2). Subduction led to the closure of the Taconic seaway (Fig. 1.2b, c), a narrow oceanic domain situated between the Baie Verte margin and Dashwoods (Waldron and van Staal 2001; Zagorevski and van Staal 2011). The Taconic orogenic cycle culminated between ca. 480 to 470 Ma in the collision between Dashwoods and the Baie Verte margin (Fig. 1.2d) and terminated between 460

and 450 Ma when the leading edge of Ganderia reached the Laurentian margin (van Staal et al. 2007; van Staal and Barr 2012).

The Penobscot orogenic cycle is solely recorded in Ganderian rocks. This cycle was partially coeval with the Taconic cycle in the peri-Laurentian realm, but it took place on the opposite side of the Iapetus Ocean near West Gondwana (Liss et al. 1994; Schultz et al. 2008; van Staal et al. 1998).

The Penobscot orogenic cycle started at ca. 515 Ma with the formation of the Penobscot magmatic arc triggered by the subduction of the Iapetus oceanic lithosphere beneath Ganderia. Between 500 and 485 Ma Ganderia was divided into two pieces by the opening of the Penobscot back-arc basin by seafloor spreading. The subsequent closure of the Penobscot back-arc basin culminated with Penobscot orogenesis between 486 and 478 (Johnson et al. 2009; van Staal 1994; Zagorevski et al. 2010).

During the Salinic orogenic cycle (440–423 Ma), Ganderia was accreted to composite Laurentia. This event started after the Taconic cycle when the leading edge of Ganderia (Popelogan-Victoria arc) collided with Laurentia (van Staal 1994; van Staal et al. 1998, 2003 Valverde-Vaquero et al. 2006a). The deformation related to the Salinic orogeny was extensive and strongly overprinted rocks located as far west as the Baie Verte margin (Cawood et al. 1994; Castonguay and Tremblay 2003).

The Acadian orogenic cycle took place mainly in the Early to Middle Devonian as a chronologically and kinematically distinct event after the Salinic orogenic cycle (van Staal 2005; van Staal et al. 2009a). Its prelude is represented by the Silurian (442–421 Ma) closure of the seaway that separated Avalonia and Ganderia (Acadian Seaway) (van Staal 2005, 2007; Valverde-

Vaquero et al. 2006a). This cycle culminated between 421 and 390 Ma with the collision of Avalonia with composite Laurentia (van Staal and Barr 2012).

The Neocadian orogenic cycle encompasses the tectonic events related to the docking and collision of composite Laurentia with Meguma, which took place from ca. 395 Ma to ca. 340 Ma (Hicks et al. 1999; Keppie et al. 2002; Reynolds et al. 2004b).

The Alleghanian cycle concluded with the oblique collision between composite Laurentia and Gondwana, which led to the formation of the supercontinent Pangea after the final closure of the Rheic Ocean (van Staal and Barr 2012, and references therein). The Alleghanian cycle started at least by 340 Ma and probably continued into the late Mississippian (Culshaw and Liesa 1997; Culshaw and Reynolds 1997; Pe-Piper et al. 2010; McKerrow et al. 2000; Torsvik and Cocks 2004; Waldron et al. 1989).

1.4 Taconic Orogeny in Northern Newfoundland

In the early 1960s, Harold Williams concluded that northern Newfoundland comprised a well-preserved cross-section of the northern Appalachian mountain belt, including two opposite-facing margins, compared to other segments of the orogen (Williams 1964). In this exceptionally exposed transect, the evidence for Taconic orogenesis is best preserved in the Baie Verte Peninsula (Williams 1977). The scarcity of Cambro-Ordovician radiometric ages and the preponderance of Silurian ages in this area has long been problematic, even casting doubt on the existence of the Taconic orogeny (Cawood, 1994), but recent radiometric ages from key localities in the Baie Verte Peninsula confirm that the Laurentian margin underwent significant tectonometamorphism during the Ordovician Taconic orogeny (Castonguay et al. 2014; van Staal et al. 2009b). During the Taconic orogenic cycle, an arc-continent collision between the Laurentian margin and the Notre

Dame arc was preceded by the closure of the Taconic seaway, which caused the obduction of the Baie Verte oceanic tract (BVOT) ophiolites onto the Laurentian margin (Fig. 2b-c) (Skulski et al. 2010).

The BVOT ophiolites (e.g. Betts Cove Complex, Pacquet Complex, Point Rousse Complex, Advocate Complex) (Fig. 1.3) represent the remnants of the supposedly narrow Taconic Seaway that was obducted onto the Baie Verte margin during the second stage of the Taconic orogeny (Taconic 2) (Fig. 1.2 c-d) (van Staal and Barr 2012). The BVOT developed between the Baie Verte margin and ribbon-like domains of continental crust located in the peri-Laurentian realm; these domains are inferred to have formed the Dashwoods microcontinent (Fig. 2b) (Waldron and van Staal, 2001). The Dashwoods microcontinent is interpreted to have rifted off the Laurentian margin in the late Neoproterozoic. During the subduction-related to the closure of the Taconic seaway, the Dashwoods microcontinent became the substrate for island-arc terranes, now represented by igneous rocks preserved within the Notre Dame arc (van Staal and Barr 2012). The Dashwoods microcontinent underwent two major magmatic pulses during the Taconic orogenic cycle: the first formed the Notre Dame arc from 489 to 477 Ma during the closure of the Taconic seaway (Fig. 1.2c, d), the second was predominantly tonalitic and occurred between 464 and 459 Ma, it is interpreted to be related to the slab break-off of the oceanic lithosphere of the downgoing slab (van Staal et al. 2007).

The Baie Verte margin contains the vestiges of a ca. 1490 Ma Pinwarian basement that was overprinted by Grenvillian tectonometamorphic imprint and a deformed cover sequence deposited from the upper Neoproterozoic to Ordovician, known as the Fleur de Lys Supergroup (de Wit and Armstrong 2014).

The Baie Verte margin formed at 615 Ma as a rifted margin, where the sedimentation of passive continental margin and foreland basin environments took place. The sedimentary sequences of the margin preserve also the record of the rift-to-drift transition, continental margin subsidence, and continent–arc collision (van Staal and Barr 2012; Waldron et al 2003). The easternmost metasedimentary units of the Baie Verte margin (e.g. Old House Cove, Rattling Brook, Birchy Complex) (Fig. 1.3) contain ultramafic slivers that are interpreted as the remnants of the leading edge of the hyperextended Baie Verte margin, whose formation is related to the separation of continental ribbons (e.g. Dashwoods) from Laurentia (Hibbard 1983, 2007; van Staal et al. 2013; Waldron and van Staal 2001).

The Mesoproterozoic basement is mainly exposed in an array of structural inliers, such as the East Pond Metamorphic Suite, which comprises Pinwarian migmatites, paragneiss, and orthogneiss overprinted by Grenvillian metamorphism (Fig. 1.3) (de Wit 1980; de Wit and Armstrong 2014; Hibbard 1983). The Middle Arm metaconglomerates unconformably overlie the basement rocks and form the base of the Fleur de Lys Supergroup (Castonguay et al. 2014).

The tectonic boundary between the Humber and Baie Verte margins and the peri-Laurentian domain is defined by the Baie Verte–Brompton Line (Fig. 1.3) a complex, protracted, brittle–ductile shear zone that now separates obducted ophiolitic crust and underlying mantle from the Laurentian continental margin (Castonguay 2014; van Staal and Barr 2012).

1.5 Eclogite and Amphibolite of the Baie Verte Margin

The basement (e.g. East Pond Metamorphic Suite) and the cover units (e.g. Middle Arm metaconglomerate, Birchy Complex, Rattling Brook Group) of the Baie Verte margin (Fig. 1.3) frequently contain centimetric to decametric amphibolite and eclogite layers, pods, lenses or boudins (Hibbard 1983). The mafic layers cross-cut the structures of their host rocks indicating

that they probably originated as dykes or sills, nevertheless, in some cases the mafic bodies have gradational contacts suggesting that their protoliths may have been mafic flows or volcanoclastic layers (Hibbard 1983). The mafic bodies are commonly extensively retrogressed to amphibolite facies metamorphic conditions, but in spite of this, they locally preserve eclogitic mineral assemblages at their cores. Such assemblages consist of garnet, omphacite, quartz, rutile, hornblende, phengite and zoisite (Castonguay et al. 2014). The metamorphic assemblage is supposed to have developed at eclogitic facies conditions, supposedly 450–500°C and 10–12 kbar, with the subsequent amphibolitization occurring at 700–750°C and 7–9 kbar (Jamieson, 1990). Willner et al. (2012) calculated significantly higher-pressure values for the metamorphic peak: 18 kbar for the garnet-mica schist of the Fleur de Lys Supergroup and 20 kbar for the eclogite pods of the East Pond Metamorphic Suite.

Castonguay et al. (2014) performed a geochronological investigation on metamorphic zircons from a partly amphibolitized eclogite of the East Pond Metamorphic Suite, which yielded a U–Pb zircon age of 465 ± 12 Ma. On the same sample, van Staal et al. (2009b) performed U–Pb geochronology of metamorphic zircon included in the rim of a garnet giving an age of 464 ± 13 Ma. These dates indicate the minimum age for the start of the Taconic collision and confirm that the early stages of this orogenic event took place in the Early to Middle Ordovician rather than during the Silurian Salinic orogeny.

Metamorphic studies and radiometric ages support the hypothesis that the Baie Verte margin, and particularly its Mesoproterozoic basement, were deeply subducted underneath the BVOT and the Notre Dame arc during the Taconic collision (Castonguay et al. 2014; de Wit and Armstrong 2014; van Staal et al. 2013). Nevertheless, there is still considerable debate about the metamorphic and structural evolution of this area, because the mafic boudins across different parts of the

peninsula seem to record contrasting metamorphic histories. Unraveling the tectonometamorphic history of these rocks should lead to a better understanding of the tectonic evolution of the Baie Verte margin during the Taconic orogeny.

1.6 Objectives

The primary objectives of this research are as follows:

The first objective is to map, describe, and gather samples of eclogitic bodies and of the geologic units that host them in the Baie Verte peninsula area. The field relationships between the different units and lithologies observed on the field were mapped and described, with a particular focus on the structural relationships between the mafic pods and their host rocks, and the structurally overlying polyphase deformed meta-sediments of the Fleur de Lys Supergroup.

The second objective is to unravel the metamorphic evolution of the eclogites, their host rocks, and the surrounding non eclogitic units (e.g. Fleur de Lys Supergroup) by performing multi-scale petrological and structural analysis and thermodynamic modelling.

The third objective is to define the timing of the main tectonometamorphic stages recorded in the eclogitic units in terms of absolute ages with geochronological techniques, in particular U-Pb on zircon, monazite, titanite, rutile, and apatite.

The fourth objective is to develop a unified tectonic model to explain the timing and the processes that led to the preservation of Taconic eclogites in the host gneisses as well their exhumation history.

Ultimately, this research results will constrain the tectonic processes active in this part of the Newfoundland Appalachians during the Taconic orogenic cycle, with broader implications for understanding the processes that control exhumation mechanisms in subduction-collisional orogens in general.

1.6 Thesis Organization

Chapters 2–4 represent three separate manuscripts in the format of journal articles. Chapter 2 provides a comprehensive description of the microstructures, petrology and mineral chemistry of the East Pond Metamorphic suite eclogites and includes thermodynamic models that define part of their P-T evolution. Chapter 3 focuses on the petrochronology of the East Pond Metamorphic suite eclogites and of crosscutting pegmatite intrusions. Integration of the results from Chapters 2 and 3 allowed a better understanding of the P-T-t-d path of the Taconic eclogites. Chapter 4 provides a comprehensive structural and metamorphic analysis of the tectono-metamorphic units that constitute the Baie Verte margin: East Pond Metamorphic Suite (EPMS) basement, EPMS cover and Fleur de Lys Supergroup (FdLS). A new tectonic framework for their Ordovician evolution is proposed. The results indicate that the three continental crustal slices that constitute the Baie Verte margin, were decoupled and juxtaposed during the Taconic subduction and exhumation along regional scale shear zones. Chapter 5 presents the conclusions of the thesis and some suggested directions for future work. Given the common geologic framework of the different chapters, some repetition in the introduction, regional geology, could not be avoided. However, modifications were made from the original submitted and unpublished manuscripts to facilitate the reading of the thesis and avoid repetition. Supplementary materials and references are presented at the end of the thesis.

1.7 Publication of Chapters

Chapter 2 is in the final stages of review at the *Journal of Metamorphic Geology*. Chapters 3 and 4 are being prepared for publication and will be submitted to the *Geologic Society of America Bulletin* and *Tectonics*, respectively.



Figure 1.1: Geologic map of the northern portion of the Appalachians that comprises Canada and part of New England (modified from van Staal and Barr, 2012). The black rectangle indicates the boundaries of the study area of this thesis. Major sutures, Early Paleozoic lithotectonic elements (coloured) and the distribution of the magmatic belts are shown. Abbreviations of Newfoundland lithostructural elements (full list in van Staal and Barr 2012) : AAT: Annieopsquotch accretionary tract; AC: Ackley granite; B: Burgeo batholith; BB: Badger belt; BBL: Baie Verte Brompton line; BE: Baie d’Espoir Group; BVOT: Baie Verte oceanic tract; C: Cripple Back–Valentine Lake plutons; CF: Cabot fault; CP: Coy Pond Complex; D: Davidsville Group; DBL: Dog Bay line; GBF: Green Bay fault; GRUB: Gander River ultrabasic belt; GZ: Gander Zone; HH: Hodges Hill Pluton; HZ: Humber Zone; LBOT: Lushs Bight oceanic tract; LR: Long Range ultramafic-mafic complex; LRF: Long Range Fault; MP: Mount Peyton pluton; NC: Noggin Cove Formation; NDSZ: Notre Dame Subzone; RIL: Red Indian line; SA: St. Anthony Complex; TE: Tetagouche Group; TP: Tally Pond Group; TU: Tulks Group; TW: Twillingate trondhjemite; VA: Victoria arc; VRF: Victoria River fault.

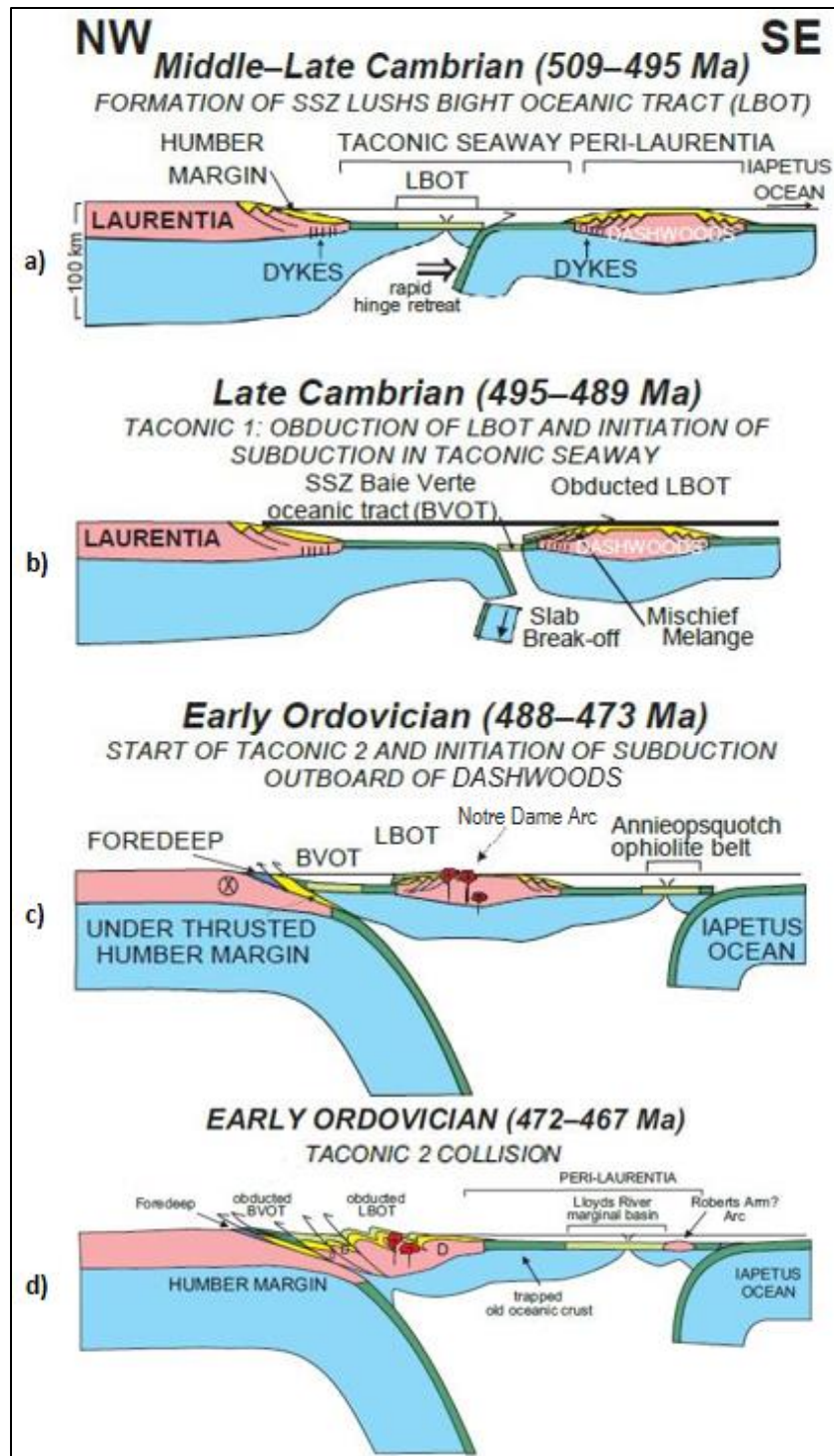


Figure 1.2: Middle Cambrian–Middle Ordovician tectonic evolution of the peri-Laurentian realm after the Subduction initiation in the Taconic seaway (Adapted from van Staal and Barr, 2012). **a)** formation the Lushs Bight oceanic tract (LBOT); **b)** obduction of LBOT onto Dashwoods during the Taconic 1 phase; **c)** west-directed subduction started outboard of Dashwoods, forming the Annieopsquotch ophiolite belt, after the first stage of collision

between promontories in the Baie Verte margin and Dashwoods; **d)** Taconic 2 collision between Dashwoods and the Baie Verte margin. Abbreviations BVOT: Baie Verte oceanic tract; LBOT: Lushs Bight oceanic tract; SSZ: suprasubduction zone; D: Dashwoods crust.

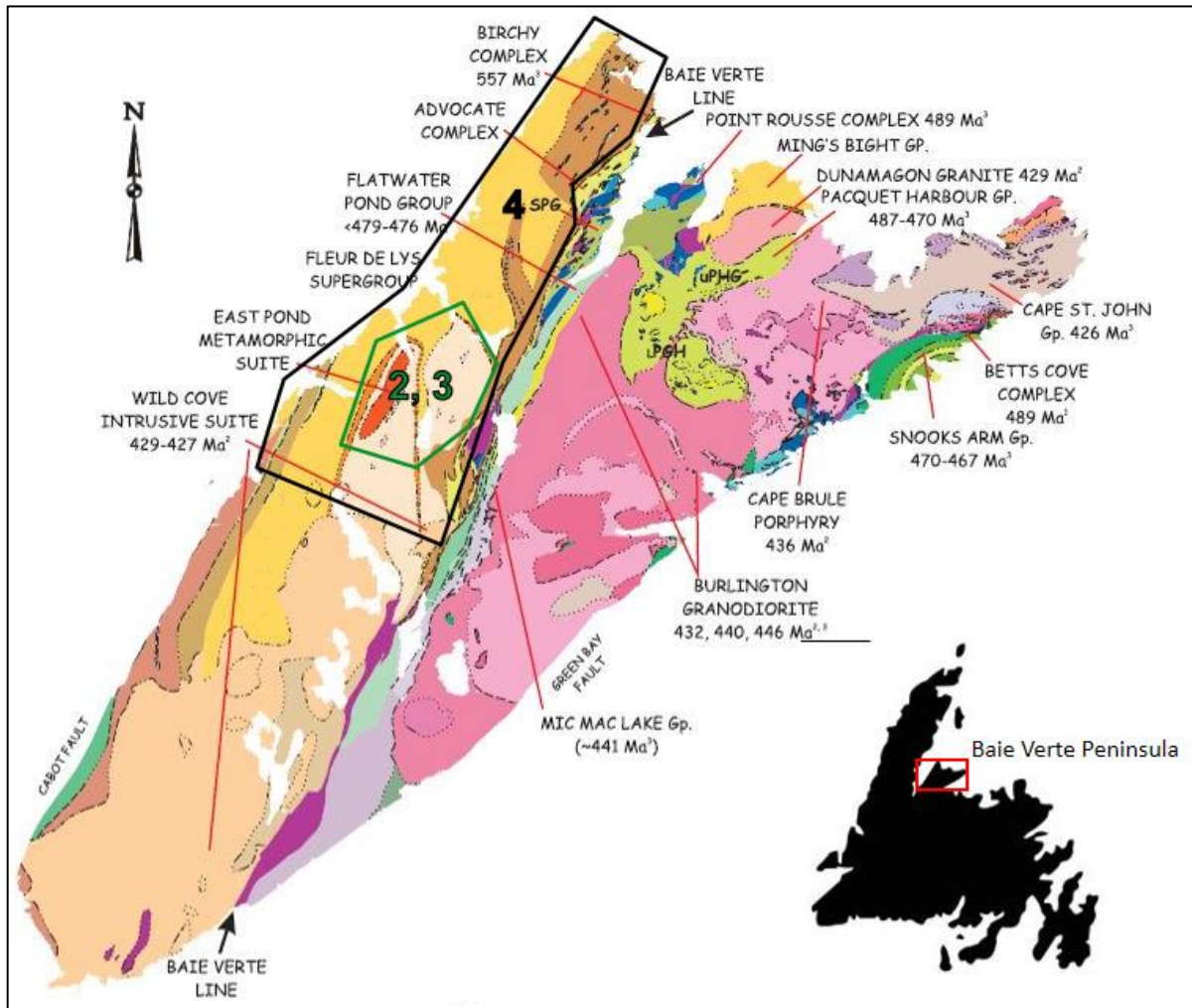


Figure 1.3: Regional geological map of Baie Verte Peninsula (adapted from Skulsky et al., 2010). The radiometric ages reported were obtained through U/Pb geochronology by Dunning and Krogh (1985), Cawood and Dunning (1993) and Skulsky et al. (2010). PHG - lower Pacquet Harbour Group; uPHG - upper Pacquet Harbour Group; SPG - Shark Point Group. The green polygon highlights the area of focus for Chapters 2 and 3, while the black polygon outlines the focus area for Chapter 4.

Chapter 2: Exhumation mechanisms of high-pressure rocks with high-temperature overprinting: insights from eclogites of the Baie Verte Peninsula, Newfoundland

Summary:

This study presents a comprehensive examination of exceptionally preserved eclogites from the Baie Verte Peninsula, Newfoundland Appalachians, which display a high-temperature (HT) overprint, thus offering insights into the metamorphic evolution and exhumation mechanisms of such terrains. Through an integrated approach combining field observations, petrographic analysis, and thermodynamic modelling, we unravel the tectonometamorphic history of the Taconic eclogites within the East Pond Metamorphic Suite. The eclogites record a complex multi-stage metamorphic path characterised by initial subduction at ~ 2.8 GPa at ~ 620 °C, followed by near-isothermal decompression to ~ 2 GPa at ~ 660 °C, and significant heating during exhumation to the metamorphic peak (~ 1.5 GPa, ~ 860 °C). We highlight the pivotal role of fluids in facilitating metamorphic reactions and influencing the rheology and buoyancy of subducting slabs. We propose a two-stage exhumation model for these eclogites: 1) initial ascent driven by buoyant forces within a low density, low-viscosity, mantle wedge; and 2) subsequent exhumation at shallower crustal levels, aided by external tectonic forces, such as shear zone displacement, erosion, or extension. The relationship between the hydration history and the reconstructed pressure-temperature-time path, featuring a β -shaped trajectory, underscores the significance of thermal perturbations and fluid migration in modeling the exhumation history of HP-UHP terrains in subduction zones.

2.1 Introduction

The global exposures of high (HP) and ultra-high-pressure (UHP) rocks in Phanerozoic orogens indicate that continental and oceanic crust can be subducted to depths >100 km (Chopin, 1984; Okay et al. 1989; Sobolev and Shatsky, 1990; Reinecke, 1998). It is generally accepted that (U)HP rocks represent subducted crust (Ernst, 1971), but despite increased recognition of high- to ultra-high-pressure terrains, the mechanisms by which these rocks return to the surface are still debated (e.g., Malusà et al., 2015).

A main challenge for understanding exhumation mechanisms lies in constraining the large number of variables that control the thermal, petrological, and rheological evolution, of subduction zones. Inferring the processes that drive exhumation of continental crustal HP–UHP material requires reconstructing pressure–temperature–time (P–T–t) paths and interpreting structural data; these data are then compared with predictions from numerical and analogue models (e.g., Jamieson et al., 2006; Kohn, 2008; Roda et al., 2012; Boutelier and Cruden 2017; Sizova et al., 2019; Faryad and Cuthbert, 2020; Regorda et al., 2021). The preservation of “hairpin”, clockwise P–T–t paths in many HP terrains indicates that the subducted rocks are typically exhumed along low geothermal gradients found in subduction zones (e.g., Pognante, 1993; Zucali and Spalla, 2011; Rebay et al., 2012; Zanoni et al., 2016; de Vries et al., 2022). Following a first stage of near-isothermal or cooling decompression, however, (U)HP rocks can record an amphibolite to high-temperature (HT) overprinting during exhumation defining “ β -shaped” P–T paths (e.g., Whitney and Dilek, 1998; Toóth et al., 2000; Brouwer et al., 2002, 2004; Orozbaev et al., 2010; Daly et al., 2012; 2022; Faryad and Žák, 2016, Baldwin et al., 2021). These P–T paths suggest a two-stage evolution, where subduction and exhumation to lower-crustal levels is followed by substantial heating. The late orogenic thermal perturbation is thought to be related to mantle upwelling

triggered by either slab break off, or slab roll back, or a combination of these processes (Sizova et al., 2012; 2019).

The migration of fluids in subduction systems also greatly impact exhumation processes. The primary source of metamorphic fluids—dominated by H₂O—in subduction zones are the hydrous mineral contained in metamorphic rocks that can be released through dehydration and partial melting reactions (Schmidt and Poli, 1998; Hacker et al., 2003; Diener and Fagereng, 2014; Zheng and Hermann, 2014; Mann and Schmidt, 2015; Walowski et al., 2015). The fluid content of subducted rocks can directly affect their density, increasing the probability of buoyancy-related exhumation mechanisms (Mukherjee and Sachan, 2009; Engvik et al., 2000), promote the development of fault systems and shear zones by reaction softening and/or rheological weakening that may accommodate exhumation (Angiboust et al., 2012; Dipple et al., 1990; Gerya and Meilick, 2011), and facilitate partial melting during decompression. This decompression melting enhances exhumation by increasing buoyancy and lubrication along interfaces of HP and UHP crustal slices (Deng et al., 2018; Labrousse et al., 2002, 2011; Schorn et al., 2021).

In this study, we combine field observations, petrographic analysis, and thermodynamic modelling to provide a new perspective on how the relative timing of fluid influx can impact the tectonic evolution of HP-UHP terrains that record HT overprinting during exhumation. We use exceptionally well-preserved eclogite samples that escaped pervasive metamorphic overprinting, and analogous eclogite that recorded several stages of amphibolite facies overprinting in the Taconic eclogites of the East Pond Metamorphic Suite (EPMS), located in the Baie Verte Peninsula (northwestern Newfoundland, Canada). We reconstruct the most complete sequence to date of the tectono-metamorphic stages recorded by the eclogites, which provides a clearer understanding of the tectonic evolution of the Taconic orogeny in the Baie Verte Peninsula. Phase

equilibrium modelling defines a retrograde β -shaped P–T–t path (Sizova et al., 2019) and we assess the role and influence of fluids on the retrograde metamorphic reactions mainly involving the breakdown of HP phases (e.g., garnet, omphacite, and phengite) and growth of Ca-Na amphibole (katophorite), and finally, by lower pressure amphibolite- and greenschist-facies assemblages.

We propose a two-stage exhumation model for the EPMS Eclogites comprising: 1) a first stage of near-isothermal decompression in eclogite facies conditions, developed in the absence of externally sourced fluids, followed by heating and exhumation to lower crustal depths; and 2) a second stage of cooling and decompression to upper crustal levels associated with an influx of external fluids. Our results have important implications for understanding the exhumation mechanisms of eclogites in the East Pond Metamorphic Suite, and eclogites with analogous P–T histories elsewhere.

2.2 Regional Geology

The Newfoundland Appalachians represent the northern termination of the Appalachian mountain belt in North America (Fig. 2.1a), which was formed mainly by the Cambrian (~515 Ma) through the Permian (~275 Ma) closure of the Iapetus and Rheic oceans and culminated with the formation of the supercontinent Pangea (Wilson 1966; Nance et al. 2008; van Staal et al. 1998, 2009a; Hibbard et al. 2010).

The Canadian Appalachians were historically divided into tectonostratigraphic zones and subzones (Williams 1979; Williams et al. 1988; Williams 1995), which were later revised by Hibbard et al. (2007) and van Staal and Barr (2012) following new insights into the provenance and tectonic setting of its rocks. Williams' (1979) Humber zone represents remnants of the Cambrian-Ordovician Laurentian margin, which in Newfoundland are now referred to as the

Humber and Baie Verte margins (Figure 2.1b); the Baie Verte margin represents an allochthonous strike-slip sliver of Laurentia's margin inferred to have been derived from the Rockall Bank northeast of Newfoundland (van Staal and Zagorevski, 2022; van Staal and Dewey, 2023; Zagorevski et al., 2023). The episodic accretion of arc terranes present in the Iapetus Ocean and Gondwana-derived microcontinents such as Ganderia and Avalonia into what is now called composite Laurentia caused the oceanward progression of the Laurentian margin (Williams, 1974; 1977; Williams et al., 1988; van Staal 2005; van Staal et al. 2009a; 2021).

The earliest accretionary stage of the Appalachian orogenic evolution is the Ordovician Taconic orogenic cycle, which occurred between the Late Cambrian and Late Ordovician (ca. 500–450 Ma). It is divided into three different evolutionary stages that encompass southeast-directed subduction of the Laurentian margin: 1) accretion of peri-Laurentian oceanic and continental arcs (upper plate); 2) slab break-off and subduction polarity reversal followed by; 3) renewed accretion (van Staal et al., 2007; Zagorevski et al., 2008). Southeast-directed subduction in northern Newfoundland led to the early Taconic accretion of Cambrian supra-subduction zone ophiolites (e.g., Lushs Bight and Baie Verte oceanic tracts) followed by collision between the Laurentian Baie Verte margin and an outboard Notre Dame arc, which was at least in part built on the peri-Laurentian Dashwoods “ribbon” (van Staal et al., 2013; Zagorevski et al., 2023). The Taconic collision in the Baie Verte margin started at ca. 480 Ma and lasted until ca. 460 Ma (Skulski et al., 2010; van Staal and Dewey, 2023).

Studies of the Taconic orogenic cycle are commonly hindered by extensive metamorphic and structural overprinting that occurred during subsequent orogenic cycles such as the Salinic ((440-423 Ma) and the Acadian (421-390 Ma) (van Staal and Barr, 2012). The strong overprinting could explain, at least in part, why preserved and, more commonly, retrogressed Taconic HP–LT

rocks such as blueschist and eclogite have been documented only in a restricted number of localities in the Appalachians, such as Connecticut (Chu et al. 2016), North Carolina (Willard and Adams, 1994; Page et al., 2003), Vermont (Laird and Albee, 1981; Laird et al., 1984; Gonzalez et al., 2020; Honsberger et al., 2020) and Newfoundland (De Wit and Strong, 1975; Jamieson, 1990; Willner et al., 2022)

Eclogites that record the Taconic subduction history are found in the Baie Verte Peninsula in northwestern Newfoundland. The Baie Verte margin comprises rock assemblages of a Late Neoproterozoic to Early Paleozoic hyperextended continental margin preserved in the Fleur de Lys Supergroup (FdLS), which formed during the opening of the Iapetus Ocean (van Staal et al., 2013). The Baie Verte margin contains the vestiges of a ca. 1490 Ma Pinwarian basement overprinted by Grenvillian tectono-metamorphism (de Wit and Armstrong, 2014) and a cover of Tonian (ca. 950 Ma) bimodal volcanic and sedimentary rocks (Strowbridge et al., 2022b), which combined constitute the EPMS. The basal part of the cover sequence of the EPMS is defined by the Middle Arm Metaconglomerate, which unconformably overlies the basement rocks (de Wit, 1980). The EPMS is mainly exposed in an array of structural inliers, which are structurally overlain by the upper Neoproterozoic to Lower Ordovician sedimentary and volcanic rocks of the Fleur de Lys Supergroup (Williams, 1969; Hibbard, 1983). The Fleur de Lys Supergroup mainly comprises marine psammitic and semipelitic schist, minor marble, and mafic layers and lenses (de Wit, 1975; Williams, 1979; Hibbard, 1983).

The tectonic boundary between the Baie Verte margin with the outboard supra-subduction zone oceanic- and microcontinental- arc terranes is defined by the Baie Verte–Brompton Line (BVBL) (Figure 2.1a, b, c) (Williams and St. Julien, 1981), a complex and long-lived brittle–ductile shear zone (e.g., Brem et al., 2007; Waldron et al., 2015) that is characterised by abundant

ophiolitic slivers that represent the early Taconic suture between the Laurentian margin and outboard intraoceanic terranes (van Staal et al., 2007; Zagorevski and van Staal, 2011; Willner et al., 2022).

2.3 Eclogite and Amphibolite of the Baie Verte Peninsula

The EPMS, and the currently overlying cover units (e.g., Middle Arm metaconglomerate, Birchy Complex, Rattling Brook Group) of the Baie Verte margin, frequently contain centimetric to decametric mafic layers, pods, lenses, or boudins (Hibbard, 1983; Skulski et al., 2017). Most mafic layers probably originated as dikes or sills based on local preservation of intrusive relationships. However, gradational contacts between country rocks and some of the mafic bodies were interpreted to represent mafic flows and/or pyroclastic layers (Hibbard 1983).

In the EPMS, mafic rocks have geochemical characteristics that are similar to mid-ocean ridge basalt and relatively uniform trace elements compositions, which suggests a common tectonic origin, whereas in the cover units of the FdLS they show more heterogeneous compositions (Massonne et al., 2022).

The eclogitic mafic boudins in the EPMS are commonly moderately to severely retrogressed to amphibolite-facies conditions with eclogite mineral assemblages mainly preserved in boudin cores. The eclogitic metamorphic assemblage was previously calculated to have formed at ~450–500°C and ~1.0–1.2 GPa by Si-in-phengite thermobarometry, with subsequent amphibolite-facies overprinting at 700–750°C and 0.7–0.9 GPa, calculated with Si-in-phengite thermobarometry and the position of the epidote amphibolite to amphibolite facies boundary (Jamieson, 1990 and references therein). Willner et al. (2012) calculated significantly higher-pressures of 2.0 GPa for the baric peak using P–T pseudosections.

The mafic bodies in the cover sequences of the Fleur de Lys Supergroup do not preserve any traces of primary eclogitic assemblage. This can be explained either by the complete retrogression of the eclogitic fabric (de Wit and Strong, 1975) or by equilibration at peak metamorphic conditions below the eclogite stability field (Jamieson, 1990).

2.4 Methods

2.4.1 *Sampling*

Samples were collected from well preserved, partially retrogressed, and completely retrogressed, mafic boudins of the EPMS. The sampling strategy was designed to take advantage of the spatial heterogeneity of the superposed structural and metamorphic overprinting identified in the field (e.g., Gosso et al., 2015). Among the 180 samples of mafic rocks collected, six were chosen for detailed petrographic and mineral chemistry analysis. These samples comprise two well-preserved eclogites (152LS1, 312LS2), three katophorite-bearing partially retrogressed eclogites (93LS1a, 93LS1c, 182LS1) and one pargasite-bearing completely retrogressed eclogite (183LS1). Polished thin sections from eclogite and amphibolite pods were used for transmitted light microscopy and for EPMA spot analyses, traverses, X-Ray maps, and LA-ICPMS analyses. Sample locations are reported in Appendix A2.

2.4.2 *Electron Microprobe Analysis*

Quantitative mineral compositions using wavelength dispersive spectroscopy were determined at Memorial University of Newfoundland using a JEOL JXA-8230 SuperProbe electron probe microanalyzer (EPMA). The EPMA spot analyses and traverses were selected on grains that constitute the sequence of key metamorphic stages, interpreted as the prograde, peak, and

retrograde stage recorded by the Baie Verte eclogites. In particular, in this work, major and minor element concentrations of garnet, amphibole, clinopyroxene, and white mica are reported.

Detailed information about the EPMA analytical conditions and the synthetic and natural standards used are summarized in Appendix A1. Briefly, amphibole and white mica were analysed for F, Na, Mg, Al, Si, K, Ca, Ti, Mn, and Fe. Clinopyroxene was analysed for Na, Mg, Al, Si, K, Ca, Ti, Mn, and Fe. Garnet was analysed for Na, Mg, Al, Si, Ca, Ti, Mn, and Fe. Rutile was analysed for Ti, Fe, and Nb. Rutile analyses were done as close as possible to the craters where LA-ICPMS analyses were previously done (see below). JEOL software was used to quantify Raw X-ray intensities using standard ZAF techniques.

EPMA X-ray maps of garnet grains preserving well defined optical zoning were acquired for Mg, Ca, Mn, Al, and Fe. Each map was generated using an accelerating voltage of 15 kV, a sample current of 250 nA, and a pixel dwell time of 150 ms. The dimensions of the map area, step size, and total counting time varied based on garnet size; maps areas ranged from 200 μm^2 to 3 mm^2 .

2.4.3 LA-ICPMS trace elements analysis of rutile

Mineral separates of rutile—collected through standard crushing, magnetic, and heavy liquid methods—from eclogite samples 93LS1a/b/c were used for in situ laser ablation inductively coupled plasma-mass spectrometry (LA-ICPMS) trace elements analyses using a Thermo Finnigan Element XR high-resolution (HR), double-focusing magnetic sector-inductively coupled-plasma mass spectrometer (HR-ICPMS), coupled to a GeoLas 193-nm Excimer laser system at the Micro Analysis Facility (MAF) at Memorial University of Newfoundland. The rutile grains were mounted in 25 mm diameter by 6 mm thick epoxy disks and polished to expose the crystal interiors.

Each rutile LA-ICPMS analysis was converted from counts to concentration using the Ti concentration determined by EPMA as the internal standard. Sixty-six rutile grains were ablated using an energy density of 4 J/cm², a 40 µm diameter spot size, and a pulse frequency of 5 Hz. For each analysis, 30 s of background measurement was followed by 60 s of laser ablation. The primary standard used was NIST 610, while NIST 612 and USGS BCR-2G were used as secondary standards. Primary and secondary standard analyses were interspersed during the trace element analyses to correct for drift, mass bias, and mass fractionation. Details and results of the LA-ICPMS analyses are reported in Appendix A5. The rutile data were reduced using the Iolite software package (v3; Paton et al., 2011).

2.4.4 Whole-Rock Compositions

Four eclogite samples (93LS1a, 93LS1c, 152LS1, and 187LS1) were analyzed for whole-rock major element concentrations. Samples were 0.8–1.5 kg in weight after having weathered and/or fractured portions removed with a diamond rock saw. Sample preparation included crushing and milling with a jaw crusher and a steel disc mill, respectively, by Activation Laboratories Ltd. (Actlabs) in Ancaster, Ontario, Canada. The samples were analysed using X-ray fluorescence (XRF) spectrometry for major elements on disks obtained through lithium borate fusion. The ratio of ferric to ferrous iron was determined by titration. The analytical results are summarized in Table A3 – I.

2.4.5 Phase Equilibria Modelling

Phase equilibrium modeling was done on two partially retrogressed eclogites, samples 93LS1a and 93LS1c. These samples were selected for modeling because they display varying degrees of

retrogression, making them better suited to constrain the retrograde P-T path compared to fresher samples (e.g., 152LS1). Pseudosections were constructed using THERIAK DOMINO vers. 2023.03.06 (de Capitani 1994, de Capitani and Petrakakis, 2010) with the Holland and Powell (2011) internally consistent thermodynamic dataset (ds62). Calculations were done in the Na₂O–CaO–K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O–TiO₂–O (NCKFMASHTO) chemical system with the following activity–composition models: amphibole (Green et al., 2016); garnet (White et al., 2014; Green et al., 2012; Diener et al., 2008); clinopyroxene with the omphacitic end-member (Green et al., 2016); orthopyroxene (White et al., 2014; Green et al., 2012; Holland and Powell, 1996); feldspar (Holland et al., 2021); ilmenite (White et al., 2000); epidote (Holland and Powell, 2011); and white mica, biotite, margarite, and chlorite (White et al., 2014). Pure phases included rutile, quartz, coesite and H₂O. All mineral abbreviations used in this contribution are from Whitney and Evans (2010).

Effective bulk compositions used for thermodynamic modelling were obtained from the XRF analyses (Table A3 – II). The content of volatile components in the samples analysed was assessed by loss on ignition technique (LOI), the value(s) obtained analytically were not used for modelling, because it is thought to have varied considerably during the metamorphic history. Thus, different hydration scenarios have been tested in the models and the ones that showed the best fit with natural data in terms of observed mineral assemblages, analysed mineral compositions and modal proportions were used. The amounts of Fe²⁺ and Fe³⁺ measured by titration analyses were used for modelling.

Isothermal, pressure vs. mol. % H₂O pseudosections were calculated for samples 93LS1a and 93LS1c at temperatures of 700, 650 and 600°C over a pressure range of 0.6 to 2 GPa. The wt. % H₂O varied between 0 for anhydrous assemblages and 2.3 % to ensure excess water in the system

to simulate fluid input from an external source. This allowed to consider a wide range of P–T paths and hydration scenarios. Amphibole compositions for these scenarios were also modelled. Garnet compositional isopleths were modelled based on a P–T pseudosection assuming 0.8 mol. % H₂O, this value corresponds to the estimated water content of the observed mineral assemblage of preserved eclogite, which contains up to 5 vol. % phengite and minor amounts of amphibole.

Different tectono-metamorphic stages were defined through the comparison of amphibole and garnet compositions modeled in pseudosections with those measured in the samples. In particular, we exploited the sensitivity of amphibole composition to changes in pressure, temperature, and hydration conditions during metamorphism (e.g., Spear, 1981; Ernst, 1988; Dale et al., 2005; Thompson and Laird, 2005; Diener et al., 2007; Uno et al., 2015), which makes amphibole a valuable tool for deciphering the evolution of subduction zone geologic settings (Rebay et al., 2012; Zucali and Spalla, 2011; Wilke et al., 2010; Palin et al., 2014; Zanoni et al., 2016; Honsberger et al., 2020; Pan et al., 2020).

2.4.6 Zr-in-Rutile Thermometry

We utilized the Zr-in-rutile geothermometer Kohn (2020), which considers the effect of pressure on temperature, to constrain the temperature conditions for the formation of the observed eclogitic fabric (see below), integrating this technique into thermodynamic modeling to construct a P–T–t path (Fig. 2.8). The Zr concentrations used were obtained from in-situ trace element LA-ICPMS analysis on rutile grain separates from samples 93LS1a//b/c.

2.5 Field Relationships

Eclogitic assemblages in the mafic boudins are preserved exclusively in the cover sequences of the EPMS (Fig. 2.1c). Amphibolite pods in the Mesoproterozoic basement do not contain omphacite or garnet; this suggests that they may have either retrogressed completely to amphibolite-facies conditions or that these rocks never reached or equilibrated to eclogite-facies metamorphic conditions.

Fresh eclogite within the core of mafic pods (Fig. 2.2a) have two superimposed foliations, S1 and S2 that developed at eclogite-facies conditions. S1 is marked by discontinuous garnet-omphacite- and quartz-rich layers ranging from 0.5 to 5 mm in width. S2 is an axial planar foliation marked by the mineral assemblage Grt+Omp+Qz+Rt+Ph+Ap. Closer to the contact with the surrounding metasedimentary host rocks, the eclogitic assemblage is variably overprinted by two main distinct amphibole-bearing fabrics. The first is characterised by katophorite (Ktp), the second is marked by pargasite (Prg). Amphibolite retrogression in the outermost parts of the mafic pods is gradational (Figs. 2.2b, c). The two retrograde assemblages are distinguished based on meso-to micro-structural and mineral chemistry characteristics presented below.

Katophorite poikiloblasts are found in the boudin cores (right side of Fig. 2.2a) where garnet and omphacite are preserved. Poikiloblasts are elongated and preferentially oriented parallel to the eclogitic S2 fabric. The presence of minerals indicative of different metamorphic facies marking the same foliation suggests that they formed during the same deformation event but under different metamorphic conditions. Eclogites located adjacent to the shear zone that separates the EPMS from the Rattling Brook Group have the highest modal proportion of katophorite which usually increases towards the rim of the pods (Fig. 2.2b).

The Prg-bearing amphibolites represent the most common type of retrogressed eclogite in the EPMS and are characterized by the following metamorphic mineral assemblage: Parg+Pl+Ep+Bt+Qz+Kfs+Ttn+Ap. When eclogitic boudin cores are preserved, the Prg-bearing assemblage is strongly developed in the eclogite rims in contact with the foliated metasedimentary host rocks. The mafic boudins are enveloped and folded F3 and enveloped by S3, which is the dominant structure at the regional scale. Hence, we interpret that the Prg-bearing amphibolites are associated with the development of S3.

The relative age relationships of amphibole growth are further indicated by a network of Prg-bearing veinlets that cross-cut the zoning defined by variable modal proportions of katophorite in the mafic pods (Fig. 2.2c).

2.6 Mineral Assemblages and Microstructures

2.6.1 Preserved Eclogites

The least altered eclogites are characterised by the mineral assemblage: Grt+Omp+Qz+Rt+Ph+Ap±Ktp. Sample 152LS1 (Fig. 2.3a) is fine-grained (~0.5 mm) with a strong foliation S2 marked by shape preferred orientation of phengite, omphacite, quartz, rutile, and apatite. Garnet exhibits inclusion-free cores, an inclusion-rich mantle, and an outer inclusion-free rim. In other samples, garnet cores may have quartz, titanite and clinozoisite inclusions. Inclusions in the garnet mantle consist of quartz and rutile. Omphacite also contains internal zoning, with cores rich in rutile and quartz inclusions, and an inclusion-free rim. Phengite is either idioblastic or subidioblastic, and typically shows no signs of internal deformation. Phengite is usually well-preserved, but may exhibit a thin rim of biotite, possibly formed during retrograde metamorphism. Rutile is found in lenticular aggregates elongate parallel to the eclogitic foliation

S2. The grains within these aggregates also exhibit shape-preferred orientation parallel to the foliation S2. Apatite is either parallel to or at a high angle to the eclogitic foliation (S2). In some eclogite samples, euhedral, twinned, 2–5 mm clinopyroxene porphyroblasts are preserved and are locally enveloped by S2. Isolated (<5 vol. %) green–blue katophorite 0.1–4 cm poikiloblasts are often observed (Fig 2.3b). Garnet inclusions have sharp or irregular boundaries when included in katophorite, while omphacite inclusions mainly display strongly resorbed grain boundaries.

2.6.2 Katophorite-bearing Partially Retrogressed Eclogites

The katophorite-bearing eclogite is a distinctive partially retrogressed rock type defined by the modal amount of katophorite exceeding 20 vol. %. Samples 93LS1a and 93LS1c (Figs. 2.3c, d) are representative of this suite; they were obtained from the core and rim of the same zoned eclogitic pod shown in Figures 2.2b and c. The mineral assemblage includes $Ktp+Ttn+Qz\pm Bt\pm Pl\pm Grt\pm Czo$. The primary distinction between these two samples is the degree of retrogression of the eclogitic fabric, which is more extensive and pervasive in sample 93LS1c.

Sample 93LS1a represents early retrogression of the eclogite-facies assemblage. Omphacite is surrounded by fine-grained symplectite of plagioclase and green amphibole. Similar to preserved eclogites, the omphacite in sample 93LS1a also contains a core rich in rutile and quartz inclusions, surrounded by an inclusion-free rim. The garnet textures also closely resemble those in fresh eclogites, exhibiting an inclusion-free core, an inclusion-rich mantle, and a clear rim. Titanite forms rims around rutile. Subidioblastic katophorite grains have shape preferred orientation parallel to the eclogitic foliation S2 and may include rutile, omphacite and garnet.

Sample 93LS1c is from the mantle of the eclogite boudin (Fig. 2.3d) and contains a relatively high proportion of katophorite (up to 35 vol. %). Omphacite is commonly absent, but its former

presence is reflected by pseudomorphs of Pl + Amp symplectite. Phengite is replaced by Bt + Pl symplectite, and rutile commonly exhibits titanite rims. Garnet in contact with Ktp and Qz shows straight boundaries. Katophorite in contact with the Amp + Pl symplectite have irregular grain boundaries. Samples of katophorite-bearing partially retrogressed eclogites can contain up to 5 vol. % of clinozoisite. Clinozoisite is commonly associated with katophorite or with the Pl + Amp symplectite. When in contact, clinozoisite and katophorite display reaction rims of plagioclase. Clinozoisite also occurs as porphyroblasts with sharp boundaries at the contact with Pl + Amp symplectite, where retrogression of the eclogitic fabric appears stronger. These textural observations, together with the absence of clinozoisite in the preserved eclogites, point to post-katophorite, and a possible post-symplectite formation growth of clinozoisite.

In the light-green, outermost rim of the eclogite boudin shown in Figures 2.3b and c, garnet shows strongly resorbed grain boundaries and epidote rims in contact with the Pl + Amp symplectite replacing omphacite. Katophorite also displays strongly irregular boundaries when in contact with the Pl + Amp symplectite. Xenoblastic amphibole (probably hornblende) is randomly oriented and locally preserves rounded symplectite inclusions, suggesting static growth of this mineral during symplectite replacement.

The eclogitic and katophorite-bearing fabrics are frequently intersected by a network of thin (< 6 mm) veins (e.g., Fig. 2.3c). These veins consist of mineral associations identical to those observed in the pargasite-bearing amphibolites described below. The veins are predominantly sharp, with surrounding omphacite showing a symplectite rim. Where katophorite poikiloblasts are cross-cut by veins, they are deformed and micro-faulted, displaying reaction textures indicated by a change in color from greenish blue to green along the vein. In the cross-cutting veins, fibrous actinolite locally replaces pargasite.

2.6.3 Pargasite-bearing Completely Retrogressed Eclogites

Samples 182LS1 and 183LS1 are representative of the progressive metamorphic overprinting of the katophorite-bearing retrogressed eclogites (Figs 2.3e, f). The inferred stable mineral assemblage in sample 182LS1 is $\text{Prg}+\text{Pl}+\text{Ep}+\text{Bt}+\text{Qz}+\text{Ttn}\pm\text{Ap}$. The most relevant microstructure indicative of the metamorphic transition from the katophorite-bearing partially retrogressed eclogites and this mineral assemblage is the growth of 0.5–2 cm pargasite, plagioclase and biotite poikiloblasts including symplectite interpreted to have formed from omphacite breakdown (Fig. 2.3e). This indicates that pargasite, plagioclase and biotite growth postdated omphacite breakdown, by replacing the first-stage retrogression product (e.g., symplectite) that developed contemporaneously with the katophorite-bearing assemblages. In the pargasite-bearing samples (Fig. 2.3E, F), garnet is pseudomorphed by aggregates of plagioclase, epidote, and biotite. Biotite in the matrix is predominantly idioblastic. Sample 183LS1 represents the final stage of retrogression recorded by the EPMS eclogites; eclogite-facies minerals (e.g., garnet and omphacite) and their early retrogression products (katophorite and $\text{Pl}+\text{Amp}$ symplectites) are completely replaced, and the minerals growing in the pargasite-bearing amphibolites display reaction textures indicating retrogression. An example of this is coarse-grained xenoblastic pargasite that is enveloped by $\text{Hbl}+\text{Act}+\text{Kfs}+\text{Pl}+\text{Qz}$ aggregates (Fig. 2.3F).

The main metamorphic evolution of the eclogites, inferred from microstructural and petrologic observations, can be summarized as follows. First, relict eclogite facies minerals (e.g., omphacite porphyroblasts) are locally pre-kinematic to S2, hence, they possibly formed during D1. Second, the eclogite-facies axial-planar foliation (early)S2, which folds S1, is marked by $\text{Grt}+\text{Omp}+\text{Qz}+\text{Rt}+\text{Ph}+\text{Ap}\pm\text{Ktp}$ and develops late during D2. Katophorite defines a foliation parallel to the eclogitic S2 indicating retrogression of eclogite to HP amphibolite conditions during

protracted D2 deformation. Incipient breakdown of high-pressure minerals (garnet, omphacite, phengite and rutile) is indicated by Pl + Bt and Pl + Amp symplectite along phengite and omphacite grain boundaries, respectively, and by titanite rims surrounding rutile. Subsequent low-pressure amphibolite-facies metamorphism during D3 overprints the katochlorite-bearing late D2 fabric. Growth of plagioclase, pargasite and biotite poikiloblasts, including retrogressive Pl+Amp symplectite, characterise the third stage of retrogression. The fourth and final, amphibolite to greenschist facies retrogression is indicated by replacement of pargasite by hornblende and actinolite.

The zoning of mafic pods (Fig. 2.3), which reflects greater degrees of amphibolitization in their outermost part, is interpreted as the consequence of fluid infiltration along grain boundaries during eclogite retrogression. The amphibole-rich vein network crosscutting the zoning in the eclogite pods, indicates that these veins record fluid pathways during a stage of lower pressure amphibolite-facies conditions following eclogite formation and retrogression through high pressure amphibolite facies conditions.

2.7 Mineral Compositions

2.7.1 Amphibole

In the EPMS eclogites, the amphibole compositions vary from sodic-calcic to calcic and are classified as katochlorite, pargasite, sadanagaite, Mg-hornblende, and actinolite (Figs. 2.4a and b; Table A4 – I). There is a positive correlation between Al a.p.f.u. (atoms per formula unit) and Na in the B-site (NaB) (Fig. 2.4e). Poikiloblastic amphibole is typically katochlorite and has the highest measured NaB contents. In the pargasite-bearing veins that crosscut preserved and partially retrogressed eclogites, two generations of pargasite, Prg1 and Prg2, were identified. Pargasite

found in the cross-cutting veins have cores (Prg1) that show a compositional trend evolving towards lower NaB composition (Prg2) (Fig. 2.4e). Amphibole rims around garnet or amphibole inclusions in some eclogite garnet rims are sanadagaite. They occur mainly in the katophorite-bearing eclogites. Hence, sanadagaite probably represents the product of the reaction of katophorite to Al-rich compositions during retrograde metamorphism rather than reflecting the composition of a generation of amphiboles formed during prograde metamorphism and garnet growth.

Completely retrogressed eclogites contain amphibole with a continuous compositional trend from pargasite, that breaks down, to form Mg-hornblende and actinolite (Fig. 2.4a). Amphiboles from this rock type have the lowest NaB content (Fig. 2.4e)

2.7.2 Omphacite

Omphacite in samples with magmatic relics, such as 312LS2, shows the lowest Jadeite (Jd) component with significant compositional variability. The jadeite component ranges from Jd₂₅ in fine-grained euhedral inclusions within other porphyroblastic cpx grains, to Jd₃₉ in the matrix omphacite delineating the eclogitic fabric (Fig. 2.4c). Omphacite has the highest jadeite composition in the well-preserved eclogites, which shows limited compositional variations within single samples but ranges from Jd₃₈ to Jd₄₇ over the suite of samples studied. Omphacite composition in partially retrogressed eclogites is Jd₃₈₋₄₀. The quadrilateral classification diagram (Fig. 2.4c) shows a systematic increase in ferrosilite composition (Fs₉ to Fs₂₃), being the highest (Fs₂₃) in katophorite bearing eclogites.

2.7.3 Garnet

Garnet varies in size between 20 μm and 3 mm in diameter. One subhedral garnet grain from partially retrogressed eclogite sample 93LS1a, measuring ca. 300 μm has and has been used for garnet isopleth modelling because it preserved the greatest compositional variation in the samples studied (Fig. 2.5). Garnet zoning is divided into a core, mantle 1, mantle 2 and an outer rim. The large grain consists of multiple core domains with high Ca and an average composition of Alm56Pyp13Grs26. Garnet core domains, when in contact, display irregular boundaries characterised by the presence of a mantle (mantle 1) with high Fe and an average composition of Alm69Pyp13Grs14. Garnet core and mantle1 are in turn enclosed in mantle 2 and rim domains, with an average composition of Alm66Pyp12Grs19 and Alm65Pyp18Grs14, respectively (Table A4 –II).

2.7.4 Phengite

Phengite grains in samples 93LS1a/b/c are up to 1.5 mm long and occur in the matrix of the preserved and partially retrogressed katochlorite-bearing eclogites. The phengite proportions varies between 0 and 5 vol. %. Compositions are usually homogeneous but may have a weak core–rim increase in the celadonite content, which varies over the range Si = 3.36–3.52 a.p.f.u. (Fig. 2.4d).

2.8 Results of Phase Equilibria Modeling

Isothermal P–M(H₂O) pseudosections were calculated for preserved and retrogressed eclogite samples to investigate the P–T–M(H₂O) conditions of amphibole growth during retrogression. Samples 93LS1a and 93LS1c, respectively from the core and the rim of the same eclogite boudin (Fig. 2.2b–c), are partially retrogressed eclogites. The eclogite rim has higher (ca. 35 vol. %) modal

proportion of katophorite than the core (ca. 12 vol. %), hence, they provide insights into the progression of eclogite retrogression (Figs. 2.3c-d). By combining the results calculated for both samples we take advantage of the petrologic heterogeneity of this eclogite, which is related to incomplete re-equilibration during hydration and the transfer of mobile components in an open system, obtaining constraints on katophorite stability that are less susceptible by local changes in the effective bulk composition. In particular, 93LS1a represents the first stage of substantial (> 20 vol. %) amphibole growth, as supported by microstructural evidence (Fig. 2.3c), hence this sample was used to model katophorite stability at higher P–T conditions. Alternatively, sample 93LS1c represents more pervasive retrogression of the eclogitic assemblage, and the incipient destabilization of katophorite, therefore, it is assumed to be more appropriate to model katophorite stability at lower P–T conditions. The starting bulk compositions obtained from XRF analyses are reported in Table A3 – II. The maximum value of H₂O has been set at 7.5 mol. % to model excess H₂O for the most hydrated compositions in the calculated P–M(H₂O) diagrams.

For each pseudosection, the following compositional isopleths were used to calculate the P–T–M(H₂O) condition of amphibole growth: Na on B *site* (Na B); Ca on B *site* (Ca B); and Na on the A *site* (Na A). These activity–composition parameters were calculated from compositions obtained from 21 amphibole EPMA analyses following the IMA2012 recommendations using the spreadsheet developed by Locock (2014). Representative compositions for each amphibole generation are shown in Table A4 – 1, and have the following ranges: Na (A) = 0.34–0.51, Na (B) = 0.28–0.34 and Ca (B) = 0.60–0.66 for sample 93LS1a, and Na (A) = 0.42–0.55, Na (B) = 0.28–0.36 and Ca (B) = 0.58–0.66 for sample 93LS1c.

Compositional isopleth intersections delimit P–M(H₂O) regions where the katophorite analysed is stable in the metamorphic mineral assemblages modeled. The amphibole generations

that follow katophorite (e.g., pargasite, hornblende, and actinolite) reflect retrogression at lower pressures and temperatures in amphibolite and greenschist facies conditions and were not modeled in this study.

The results of amphibole isopleth modelling of sample 93LS1a show that katophorite is stable at *c.* 700° C at 1.3–1.4 GPa for a bulk composition with 0.3–0.76 mol. % H₂O (Fig. 2.6a). At these conditions, the metamorphic association predicted is Amp+Cpx+Grt+Pl+Bt+Qz+Ru+Ilm, which is consistent with the observed assemblage, where Amp+Pl symplectites replace omphacite, and incipient Pl+Bt symplectites replace phengite. The results from this model predict that rutile is stable during the first stages of katophorite growth, consistent with microstructural observations such as rutile without titanite rims included in katophorite. At 650° C and 1.2–1.3 GPa (and bulk rock H₂O of 0.3–1.6 mol. %), katophorite is part of a modelled assemblage defined by Amp+Cpx+Grt+Pl+Bt+Qz+Ilm (Fig. 2.6b). Katophorite in sample 93LS1c is predicted to be stable at 600° C at ~1.2 GPa for a bulk rock H₂O content of 2.1–3.9 mol. % over three phase assemblage fields characterised by Amp+Cpx+Grt+Pl+Bt+Qz+Ilm±Ru±Ttn (Fig. 2.6b). The results from this model predict the breakdown of rutile and titanite growth with increasing water content, which is compatible with titanite rims associated to katophorite modal increase in the sample (Fig. 2.3c).

Garnet compositional variability in sample 93LS1a is expressed in terms of molar proportions of pyrope (X_{py}: Mg / [Mg + Fe + Ca]), grossular (X_{grs}: Ca / [Mg + Fe + Ca]) and almandine (X_{alm}: Fe / [Mg + Fe + Ca]) and these are plotted in Figure 2.7. Representative analyses of the core, mantles, and rim of garnet (Fig. 5) are shown in Table A4 – II. The modeling does not reproduce the garnet core compositions; this is probably because of their very low almandine content. Mineral inclusions in the garnet cores (e.g., quartz and titanite) are also not diagnostic of

specific P–T conditions. Therefore, the prograde path of the eclogites up to the maximum pressure is unconstrained.

The garnet mantle 1 composition has the highest X_{alm} contents (Fig. 2.5) and these correspond to calculated conditions of 580–660 °C at 2.5–3.1 GPa (Fig. 2.7); this is interpreted as the peak pressure. Garnet mantle 2 compositions are consistent with 640–690 °C and 1.8–2.2 GPa (Fig. 2.7). The outermost rim (e.g., rim 3) has compositional isopleths that correspond to a narrow P–T window at 850–875 °C and 1.5–1.6 GPa.

2.8.1 *Si-in-Phengite Barometry*

The phengite isopleths calculations, based on the compositions analyzed in phengite marking the S2 foliation, were done on the same pseudosection used for garnet isopleth modeling, and expressed in terms of Si a.p.f.u (Fig. 2.8). Phengite isopleths modelling constrains a pressure interval between ~1.7 and 2.4 GPa.

2.8.2 *Zr-in-Rutile Thermometry*

The application of the combined model of Kohn (2020) for Zr-in-rutile thermometry requires assumed pressures. We use the results of silica-in-phengite barometry that have values between 1.7 and 2.2 GPa. Phengite is elongated in the S2 foliation along with rutile, omphacite, garnet and quartz. Therefore, this is an appropriate estimate of pressure associated with eclogite-facies metamorphism. Of the 66 analyses of rutile, 12 were discarded due to contamination by zircon nano-to micro-inclusions indicated by elevated Hf values. The remaining 54 analyses yield Zr concentrations of 94–271 ppm. At the assumed pressures (1.7–2.2 GPa), these concentrations correspond to temperatures of ~550–650 °C (Fig. 2.8).

2.9 P–T Evolution

Based on the results of microstructural analysis, phase equilibria modelling, Si-in-phengite thermometry, and Zr-in-rutile thermometry, a best-fit retrograde P–T path is shown in Figure 2.8. Peak pressures (~2.8 GPa) are at the boundary between HP and UHP conditions as indicated by compositional isopleths calculated for garnet mantle 1. Decompression from peak pressure includes three main stages: 1) near-isothermal decompression from peak pressure; 2) decompression and heating to peak temperature; and 3) decompression and cooling to greenschist facies conditions.

The first stage of decompression includes a segment of near-isothermal decompression to eclogite-facies conditions constrained by garnet isopleths, Zr-in-rutile thermometry and Si-in-phengite at ~650 °C and ~2 GPa, respectively. This stage is associated with eclogite-facies assemblage of Grt+Omp+Qz+Rt+Ph+Ap±Ktp developed during D2.

The second stage of decompression accompanied by heating to ~860 °C at ~1.5 GPa (peak heating), which is defined by garnet outer rim isopleths (Fig. 2.8). Both phase equilibria modeling and petrographic observations suggest that orthopyroxene did not form at these peak temperature conditions even though granulite-facies conditions were potentially reached.

The third stage is a decrease in temperature from peak T associated with decompression and hydration; this led to a modal increase of katochlorite (up to 35 vol. %) between 700 and 600 °C, and to the complete replacement of omphacite by Pl + Amp symplectite. The final stages of retrogression are depicted by the P–T conditions given by the growth of the amphibolite facies assemblage during D3: Parg+Pl+Ep+Bt+Qz+Kfs+Ttn±Ap, which in turn was overprinted by greenschist facies characterised by actinolite. The latter greenschist-facies conditions are interpreted to mark the final exhumation stage.

In summary, the post-peak metamorphic history of the EPMS eclogites followed a clockwise “ β -shaped” P–T path including decompression with both cooling and subsequent heating events (Fig. 2.8).

2.10 Discussion

2.10.1 *Limitations and Assumptions of Phase Equilibria Modelling*

Phase equilibria modelling requires a simplification of complex natural systems, implying a degree of disregard of many uncertainties (e.g., Palin et al., 2016; Yakymchuk et al., 2017). Among the major uncertainties are the systematic limitations in the thermodynamic properties of end-member phases and the activity–composition models available in the thermodynamic databases (Holland and Powell, 2011; White et al., 2014). Of equal importance is the assumption that equilibrium was attained in the metamorphic assemblages observed. For example, the growth of zoned minerals—especially garnet—that affect the effective bulk composition reflects disequilibrium during a protracted metamorphic evolution (e.g., Caddick and Thompson, 2008). Microstructures such as symplectites and coronae may reflect variations in chemical potential, which are also non-equilibrium features (e.g., White et al., 2008; Li et al., 2022).

In the EPMS eclogites, disequilibrium textures have been observed in all the metamorphic stages that we were able to reconstruct. To minimize this source of uncertainty, the samples used for bulk rock analysis were selected and prepared by isolating rock volumes that preserved the least possible number of metamorphic assemblages, and least amount of weathering, to approximate the whole rock composition that is interpreted to be associated with a specific part of the metamorphic evolution of the system. The changes that zoned garnet growth induces in the reactive bulk composition can be approximated using garnet fractionation models (e.g., Evans,

2004). We did not use fractionation models because the garnet samples studied showed well-constrained intersections between rim isopleths and poor intersections between core isopleths; therefore, crystal fractionation was interpreted to not be a source of disequilibrium (e.g., Evans, 2004). A possible reason for the well-constrained rim intersections is the participation of garnet cores in metamorphic reactions. Textural evidence supports this hypothesis because “atoll-like” garnets and fractured garnet cores containing younger metamorphic retrograde assemblages were commonly observed in the studied samples. The poor intersections between core isopleths may imply that the reactive bulk composition at the time of their growth had deviated along the P–T path.

In several cases, phase equilibria modelling predicted that two clinopyroxenes were stable in the same assemblage. This may reflect uncertainties in the closure of the solvus between these clinopyroxenes, and/or unresolved issues with the activity–composition models of omphacitic clinopyroxene (e.g., Green et al., 2007). These fields, however were outside of the P–T space of direct relevance to the best-fit P–T path for our samples. This suggests that some uncertainties remain in the clinopyroxene activity–composition models (c.f., Forshaw et al. 2019). Hence, we did not use compositional isopleths of clinopyroxene in our estimates, but we acknowledge that this may have consequences for modelled garnet and possibly amphibole compositions. Nevertheless, the well constrained intersection of garnet isopleths from particular zones (e.g., mantle 1, mantle 2, rim) are consistent with P-T constraints from other thermobarometric methods and the observed inclusion assemblages, suggesting that the garnet compositions modeled are a geologically reasonable reflection of the garnet compositions measured.

Reaction “overstepping” refers to the delay in the onset of a mineral reaction beyond the conditions predicted by equilibrium thermodynamics (Fisher, 1981). This phenomenon occurs

when a reaction does not initiate immediately upon reaching the P-T conditions under which it is thermodynamically stable, which leads to a discrepancy between predicted and actual reaction conditions (Spear and Wolfe, 2019). In the present study, overstepping during garnet formation poses a potential challenge in accurately estimating P–T conditions. Traditional models, predicated on the assumption of constant growth conditions, may not fully capture the complexities introduced by overstepping and lead to incorrect interpretations of the metamorphic conditions. Future endeavors to consider and prevent the effects of overstepping could involve incorporating kinetic factors into the models to account for the deviation from equilibrium thermodynamic conditions. This can include adjusting the models to account for the rates of nucleation and growth of minerals, which are influenced by overstepping (Wolfe and Spear, 2018; Faryad et al., 2022). For the EPMS eclogites, the similarities between phase equilibrium models and mineral thermobarometry (e.g., Zr-in-rutile, Si-in-phengite) suggest that reaction overstepping did not have a major influence on the samples in the present study.

The pseudosection presented in Figure 2.7 predicts biotite stability and excess H₂O in the field where garnet isopleths intersect at ca. ~650 °C and ~2 GPa. This contrasts with the petrologic observation that phengite is the stable K-bearing hydrous mineral, under those conditions, marking the foliation S2. This discrepancy has been previously observed and studied in detail by Nakamura (2003) and Massonne (2024). Those authors suggest that biotite is, in principle, a stable phase in eclogites with a basaltic bulk composition with relatively low Ca, Al and Fe³⁺, and high K and Fe²⁺ contents. Those authors also document, however, the inconsistency between observed vs modeled assemblages and analyzed vs modeled compositions of biotite at high pressure conditions.

The problem of the eclogitic nature of biotite can be attributed to complexities that are not yet fully understood, including: 1) the lack of experimental calibration data for biotite behaviour

at high pressure; 2) the interplay between biotite and other hydrous phases that may be present in eclogites (e.g., amphibole); and 3) the assumption of pure H₂O when supercritical fluids at eclogite-facies conditions may contain an appreciable amount of dissolved cations (e.g., Manning, 2004). In our model, the amount of free water and biotite predicted in the fields where garnet isopleths intersect are 0.2 and 3 vol. %, respectively. We consider these relatively minor amounts of biotite to be within the uncertainties of the thermodynamic models; they are not expected to significantly affect the P-T estimates and the interpretations regarding the hydration history of the eclogites.

In consideration of the uncertainties discussed above, the best-fit exhumation P–T path accounts for all of the key observations including the measured mineral compositions for both major (e.g., garnet, amphibole) and accessory (e.g., titanite) minerals. Therefore, we consider the predicted P–T path to be a reasonable approximation for the exhumation history of the EPMS eclogite.

2.10.2 *P–T–t path*

Petro-structural analysis and thermodynamic modelling of the Taconic eclogites in the Baie Verte Peninsula, in the Newfoundland Appalachians, highlight a complex metamorphic history recording subduction and subsequent exhumation. Although the first part of the metamorphic P–T path (Fig. 2.8) defines the baric peak at ~2.8 GPa, which partly overlaps with UHP conditions in the coesite stability field, coesite is lacking in the peak mineral assemblage of EPMS eclogites. The presence of coesite, however, has been recently documented in other parts of the Taconic orogen in North America (Gonzalez et al., 2020). Therefore, based on the estimated peak P–T conditions shown in Fig. 2.8, the Taconic eclogites in the Newfoundland Appalachians likely

reached subduction depths around 90 km, within the stability field of coesite, even though direct evidence of coesite has not been found in the EPMS eclogites. Constraints on the timing of eclogite-facies metamorphism of the EPMS eclogites are presently provided by whole rock Lu–Hf (464.3 ± 1.4 Ma) and Sm–Nd (456 ± 11 Ma) garnet-omphacite isochrons reported in Strowbridge et al. (unpublished data; 2022a) and a U–Pb zircon date of 465 ± 12 Ma obtained from a sample of eclogite that was partially retrogressed to amphibolite facies conditions (Castonguay et al., 2014).

The least altered deformed and foliated EPMS eclogites probably formed during the first stages of isothermal decompression. This is supported by the observation that the formation conditions of the eclogite minerals that define the well-preserved S2 foliation (Figs. 2.3a, b, c) are constrained at ~2 GPa and ~660 °C through the integrated modeling of phengite, rutile, and by garnet thermobarometry.

Peak temperature conditions typical of granulite facies were reached during exhumation at about 860 °C and 1.5 GPa. Such high temperature conditions are well documented in many continental exhumed (U)HP terrains, whose ascent is commonly aided by adjacent lower density buoyant material, such as partially molten felsic rocks (e.g., Jouffray et al., 2020 Möller et al., 2015). Although EPMS eclogites do not show clear field or petrographic evidence of partial melting, there is evidence of partial melting in the enveloping metasedimentary rocks, including leucosome with garnet, which is diagnostic field evidence of hydrate-breakdown melting in migmatites (e.g. Johnson et al., 2021). High-temperature overprinting of (U)HP rocks that is not characterized by granulite facies index minerals has been documented through pseudosection modeling in other high-pressure terrains, such as the Western Gneiss Region of Norway (Engvik et al., 2018) and the Tien Shan Mountains in Central Asia (Orozbaev et al., 2010). These authors

documented compositional profiles in garnet that show an increase of Mg and a decrease in Ca towards the rim, which are very similar to the garnets measured here (Fig. 2.5); these trends were interpreted as prograde garnet growth under increasing temperatures and, in the case of the Western Gneiss Region, during decompression melting.

The growth of high-pressure amphibolite-facies assemblages characterizes the exhumation path at lithospheric depths. Macro- and micro-structural and mineral compositional evidence support the hypothesis that the katophorite-bearing assemblages formed after the peak metamorphism and before the pargasite-bearing low pressure amphibolite-facies overprint (Fig. 2.3e) and, therefore, it is interpreted to be directly related to metamorphism developed during exhumation of the EPMS eclogites. Silurian titanite dates of 429.4 ± 9.5 Ma (Strowbridge et al., unpublished data; 2022a), and 429–417 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ dates (Castonguay et al., unpublished data, 2010) provide maximum age constraints for eclogite exhumation.

2.10.3 Hydration During Exhumation

High modal proportions of katophorite in the eclogites (Figs. 3c, d) indicate significant fluid infiltration during retrograde metamorphism. This suggests that fluid influx played a crucial role in promoting the retrograde metamorphic reactions and facilitating deformation associated with exhumation. Notably, the mineral assemblage zoning in partially retrogressed mafic boudins is defined by the variable modes of katophorite and actinolite, which increases towards pod rims. The gradational transition from pristine eclogite to amphibole-bearing assemblages suggests that katophorite formation resulted from diffusive fluid percolation along grain boundaries, progressing inward from the outer edges of the mafic pods (e.g., Ferrando et al., 2007). In contrast, pargasite predominantly occurs in the most external parts of the pods or in veins which crosscut

the zones with abundant katophorite (Fig. 2.2c), hence, this metamorphic stage is thought to be related to later external fluid injection at lower pressures that is not considered as part of the initial eclogite exhumation.

Massonne (2024) inferred that there had been eclogitic-facies biotite porphyroblast growth in the EPMS. Our observations indicate that biotite grows, at first, as thin rims surrounding phengite in the preserved eclogites. Subsequently, biotite forms through the complete replacement of phengite by Bt+Pl symplectites in the katophorite-bearing retrogressed eclogites. Finally, biotite porphyroblasts characterize the pargasite-bearing retrogressed eclogites. Our petrologic observations support the hypothesis that biotite and Ca-amphibole (pargasite) growth is related to the same metamorphic stage (Fig. 2.3e). The crosscutting relationships of veins containing both pargasite and biotite and the eclogites, however, suggests that biotite porphyroblasts growth is unrelated to eclogite formation and their early exhumation history. Instead, our observations are coherent with late-exhumation growth biotite porphyroblasts.

2.10.4 Heat and Fluids: Implications for Eclogite Exhumation Mechanisms

The P–T path reconstructed for the EPMS eclogites (Fig. 2.8) provides insights into the evolution of the thermal structure of the subduction system. The P–T path is β -shaped, which has also been documented in many exhumed (U)HP terrains (e.g., Kurz et al., 1998; Wiederkehr et al., 2008; Wilke et al., 2010; Whitney et al., 2011; Liu et al., 2013; Perraki and Faryad, 2014; Faryad and Fišera, 2015; Faryad and Žák, 2016; Baldwin et al., 2021). The P–T path of EPMS eclogites indicates a two-stage exhumation marked by a multistage decompression path (Fig. 2.8). Early exhumation is characterised by isothermal decompression, transitioning into decompression with an increase in temperature; this heating may have been caused by mantle upwelling resulting from

slab rollback, steepening, or break-off. Such mantle upwelling probably causes partial melting of subducted rocks (Gerya et al., 2002; Warren, 2008; Sizova et al., 2019). The first exhumation stage, from peak pressure to peak temperature, is primarily driven by buoyancy forces facilitating the rapid ascent of continental material from mantle depths to lower crustal levels through low viscosity channels at the slab-mantle interface (Rubatto and Hermann, 2001; Hattori, 2007; Sizova et al., 2012; Engvik, 2018). Subsequently, a second exhumation stage characterized by a slower exhumation rate, during which decompression is associated to cooling, may be driven by external forces such as extension and/or erosional denudation following collision-related thickening (Butler, 2018; Escher and Beaumont, 1997; Kurz and Froitzheim, 2002).

The hydration history of the eclogites allows for a more complete description of the subduction environment. In particular, petrologic observations and pseudosection modeling suggests that the water content of the eclogites remained nearly constant (ca. 0.8 vol. %) during exhumation from mantle to lower crustal depths, where they experienced the HT peak. The appearance of increasing proportions of hydrous minerals during decompression and cooling at crustal levels indicate influx of fluids and hydration up to ca. 3.9 mol. % H₂O. The occurrence of rocks that record substantial externally-sourced fluid influx, represented by katochlorite growth (Figs. 2.3b, c, d), is limited to areas adjacent to a regional scale shear zone separating the East Pond Metamorphic Suite and the Rattling Brook Group (Fig. 2.1c). This potentially lubricated and weakened tectonic boundary could have allowed thrusting and further exhumation of high-pressure rocks.

We favour a two-stage exhumation model for three reasons:

- 1) First, numerical simulations aimed to model P–T paths akin to those reconstructed in this study, suggest the necessity for continental subduction reaching significant depths (> ~90 km).

These simulations indicate that subduction of thinned continental crust at the leading edge of a continental margin is generally capable of reaching greater depths than margins characterised by an abrupt transition between continental and oceanic crust (Sizova et al., 2012). These conditions are consistent with the tectonic evolution reconstructed for the Taconic orogenic cycle. This cycle began with the protracted subduction of Laurentia's wide, hyperextended continental margin characterised by a mixture of sedimentary rocks, less buoyant mafic rocks and associated exhumed mantle (van Staal et al., 2013), which formed a semi-oceanic seaway between the less extended margin and the outboard Dashwoods terrane (van Staal and Dewey, 2023). These characteristics highlight the potential for parts of the Early-Paleozoic Laurentian margin (Baie Verte margin) to have been subducted to depths of ca. 90 km.

2) Vertical extrusion of a major slice of partially eclogitised crustal rocks may be facilitated by a low viscosity ascent channel that was rheologically weakened by ascending melts and fluids (Faccenda et al., 2008; Gerya et al., 2008; Warren et al., 2008; Angiboust et al., 2012; Labrousse et al., 2015; Faryad and Cuthbert, 2020). Such an ascent channel can accommodate exhumation of subducted rocks from mantle depths to sub-crustal levels, and the juxtaposition of lithospheric and asthenosphere material (Sizova et al., 2012). This type of environment can be responsible for the heating of continental (U)HP rocks and triggering partial melting (Bouilhol et al., 2015; Li and Gerya, 2009). The presence of granitic melts in the EPMS and evidence of partial melting in the metasedimentary host rocks that envelop the eclogites, could have produced zones of significant structural weakening and made the subducted rocks more buoyant, which in turn promoted their ascent (Scambelluri and Philippot, 2001). Hence, the reconstructed P–T path is consistent with numerical models and with studies of natural data from localities characterised by similar β -shaped

P–T paths are interpreted to be related to exhumation mechanisms such as vertical tectonic extrusion (e.g., Faryad and Cuthbert, 2020; Sizova et al., 2019).

3) Evidence for cooling during decompression of the EPMS at higher crustal levels (Fig. 2.8) suggests that late exhumation may be driven mainly by external forces rather than buoyant rise of hot crustal lower density material. Crustal-scale thrusting-related shear zones may facilitate uplift of HP units in collisional orogens if they are coeval with removal of their structural cover by erosion and/or extension (Escher and Beaumont, 1997; Ring et al., 1999; Ernst, 2001). The spatial association of katochlorite-bearing retrogressed eclogites with crustal scale shear zones (Fig. 2.1c) near the structural boundaries of the EPMS inliers supports such a hypothesis. The abundance of deformed quartz veins in the shear zones suggests that fluid flow enhanced retrogression and weakened the sheared rocks (Miller et al., 2002; Oliot et al., 2010; Sizova et al., 2010).

2.10.5 Tectonic Evolution and Global Correlations

The P–T path presented here is consistent with the tectonic framework concerning the subduction and collision of the Laurentian margin with the Dashwoods terrane during the Taconic orogeny (van Staal et al., 2007; Castonguay et al., 2014). The results from the present study provide further geothermobarometric constraints on the metamorphic evolution of the EPMS eclogite of the Baie Verte margin (Fig. 2.1c), which are critical for integrating the tectonometamorphic history with the large-scale tectonic processes accompanying the Taconic orogenic cycle in this part of Newfoundland and also in the northern Appalachians. Particularly, the importance of the late Taconic slab break-off for the thermal evolution of the rocks is highlighted, whereas unbending of the remaining part of the broken slab during its rebound (van Agtmaal et al., 2023) may have driven the late exhumation of the EPMS.

Establishing the relationships between retrograde amphibole growth and regional structures developed during D2 and D3 (Figs. 2.2, 2.3) is crucial for understanding the Taconic orogeny and for recognizing tectonometamorphic overprinting related to subsequent events. In particular, we suggest that the development of katophorite (Figs. 2.3b, c, d) marks exhumation probably related to the Taconic orogenic cycle. By contrast, the development of pargasite-bearing retrogressed eclogites (Figs. 2.3e, f) is related to a metamorphic event followed by eclogite retrogression to greenschist facies conditions, possibly related either to late Taconic collision or to the Silurian Salinic orogeny. Future studies focussing on geochronological investigations on crosscutting dikes and retrograde metamorphism could help constrain the timing and possibly the duration of collision and exhumation processes.

The Irish and Scottish Caledonides, like the Taconic orogen formed during the Early to Middle Ordovician collision between the extended Grampian terrane at the Laurentian margin's leading edge and an outboard arc terrane. Both the Taconic orogen and the Grampian tract preserve records of subduction, followed by slab break off, and subduction polarity reversal (van Staal and Dewey, 2023). High-pressure granulite facies metamorphism at ca. 470 Ma following the eclogitic-facies baric peak dated at ca. 473 Ma has been documented in the Slieve Wood terrane in northwestern Ireland, located along the southwest margin of the Grampian belt (Daly et al., 2012; 2022). Evidence for analogous high-temperature overprinting experienced by the EPMS eclogite presented and discussed in this study, further cements the broadly contemporaneous metamorphic evolution of the Grampian and the Taconic orogens.

2.11 Conclusions

Eclogite boudins in the East Pond Metamorphic Suite record a multi-stage retrograde evolution with a β -shaped P–T path and a baric peak at ~ 2.8 GPa and ~ 620 °C. Peak pressure was followed by a multi-stage exhumation history starting with near-isothermal exhumation to ~ 2 GPa, ~ 660 °C, which was followed by heating at ~ 860 °C, ~ 1.5 GPa, and then by a post HT stage.

This evolution is interpreted to record exhumation to crustal levels along with the hydration and break-down of eclogite-facies mineral assemblages as well as development of high pressure katochlorite-bearing amphibolite assemblages. This P–T path reflects a two-stage exhumation: 1) Initial ascent from mantle depth dominated by buoyancy (e.g., vertical extrusion) followed by; 2) exhumation to shallower crustal levels driven by displacement along the regional tectonic boundaries, such as the shear zones between EPMS and Fleur de Lys and between the EPMS and Rattling Brook Group. The documented metamorphic assemblages and P–T path suggest that Taconic subduction and exhumation of the hyperextended Baie Verte margin in the Newfoundland Appalachians, followed the closure of the segment of the Iapetus Ocean between Laurentia and the outboard Notre Dame arc. Hence, this segment of the Taconic orogen in northwestern Newfoundland is a case study of geodynamic processes associated with deep subduction and exhumation of hyperextended margins.

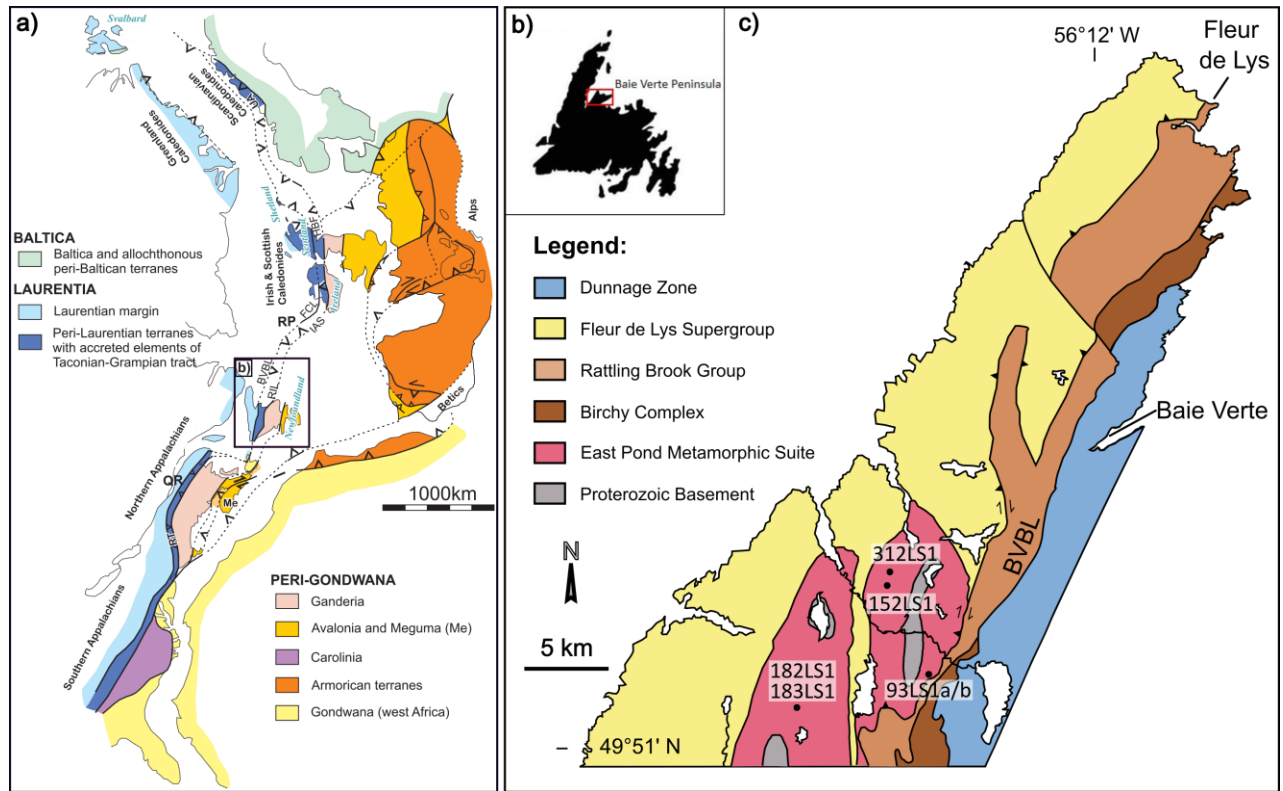


Figure 2.1: (a) Geological Map of the Appalachian-Caledonian orogenic belt (modified from van Staal and Dewey, 2023). (b) Map of Newfoundland showing the location of the Baie Verte Peninsula. (c) Simplified geology of the Baie Verte Peninsula (modified from Skulski et al., 2010). Sample locations are shown by the black dots. Abbreviations: BVBL = Baie Verte Brompton Line; FCL = Fairhead Clew Bay Line; HBF = Highland Boundary Fault; IAS = Iapetus suture; QR = Quebec re-entrant; RIL, Red Indian Line; RP = Rockall promontory; UA = Upper Allochthon.

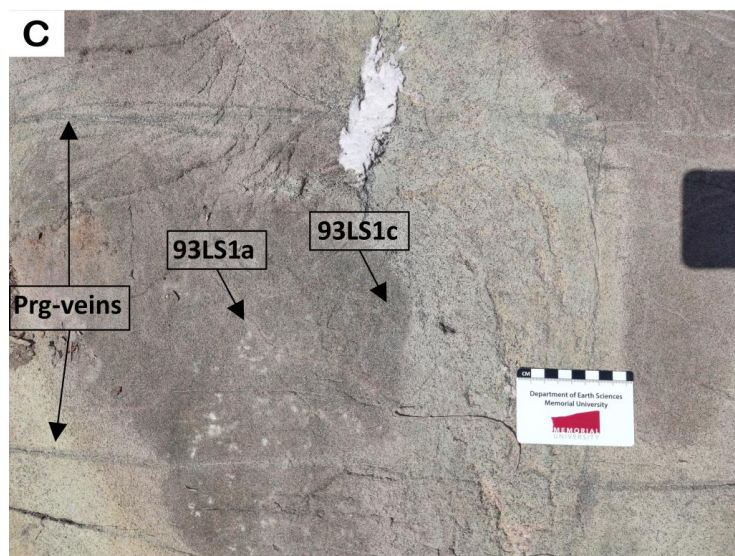
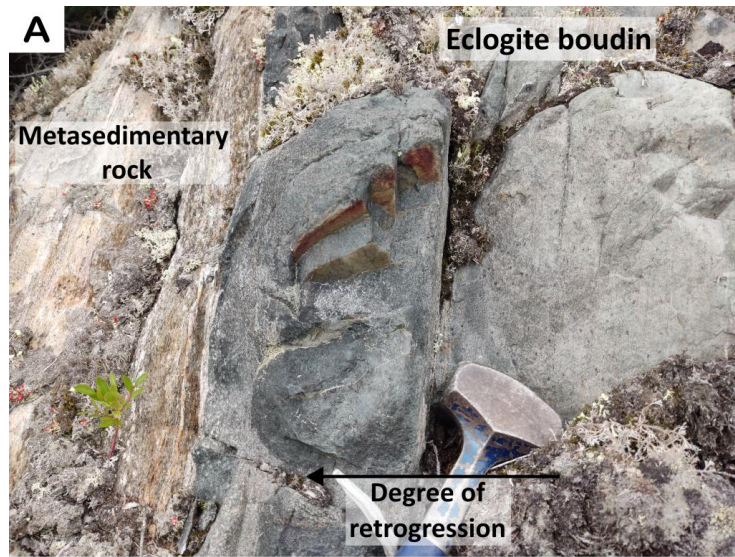


Figure 2.2: **(A)** Eclogite boudin hosted in EPMS metasediments. The arrow indicates the increase in the degree of retrogression, in particular, the preserved eclogite assemblage in the core of the mafic boudin (right side) is gradually replaced by amphibolite towards the contact with the metasedimentary host rock (left side). **(B)** Zoned eclogite outcrop. The darker patches highlight areas where the eclogitic assemblage comprising garnet, omphacite, quartz, rutile and katophorite is well-preserved. In the lighter-coloured portions eclogite is replaced by plagioclase and green amphibole. **(C)** Detail of the outcrop are shown in (B). Note the katophorite-rich rim (sample 93LS1C) developed around a katophorite-bearing eclogite (sample 93LS1a), and pargasite veins cross-cutting the eclogitic and the katophorite-bearing fabrics.

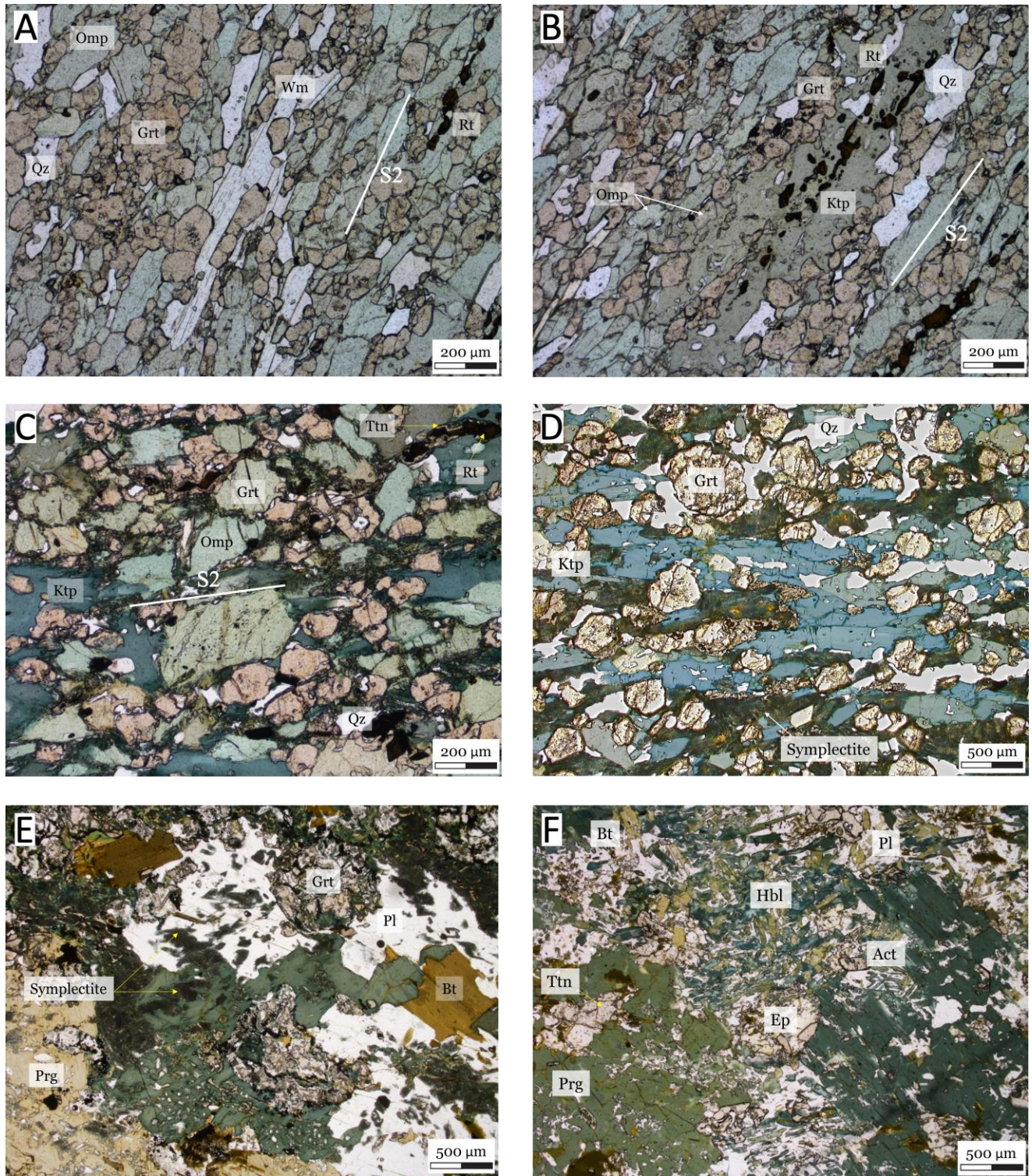


Figure 2.3: Microphotographs of eclogite showing an increasing degree of retrogression from A) to F). **A)** Sample 152LS1: preserved eclogite in which the eclogitic fabric S2 is marked by Omp+Grt+Phg+Qz+Ru±Ap. **B)** Sample 152LS1: poikilitic katophorite grows replacing Omph. **C)**

Sample 93LS1a: katophorite modal abundance increases, titanite rims replace rutile, incipient Amp+Pl symplectite formation at grain boundaries. **D)** Sample 93LS1c: katophorite modal increase is associated with the formation of Amp+Pl, Bt+Pl symplectites and titanite rims surrounding omphacite, phengite and rutile, respectively. **E)** Sample 182LS1: Pargasite and plagioclase poikiloblasts and biotite grow resorbing the Amp+Pl symplectites formed after Omp breakdown. Ep+Pl+Opq pseudomorphic aggregates replace garnet. **F)** Sample 183LS1: Subidioblastic pargasite crystals are replaced at the grain boundaries by Hbl-Act-Pl-Kfs aggregates.

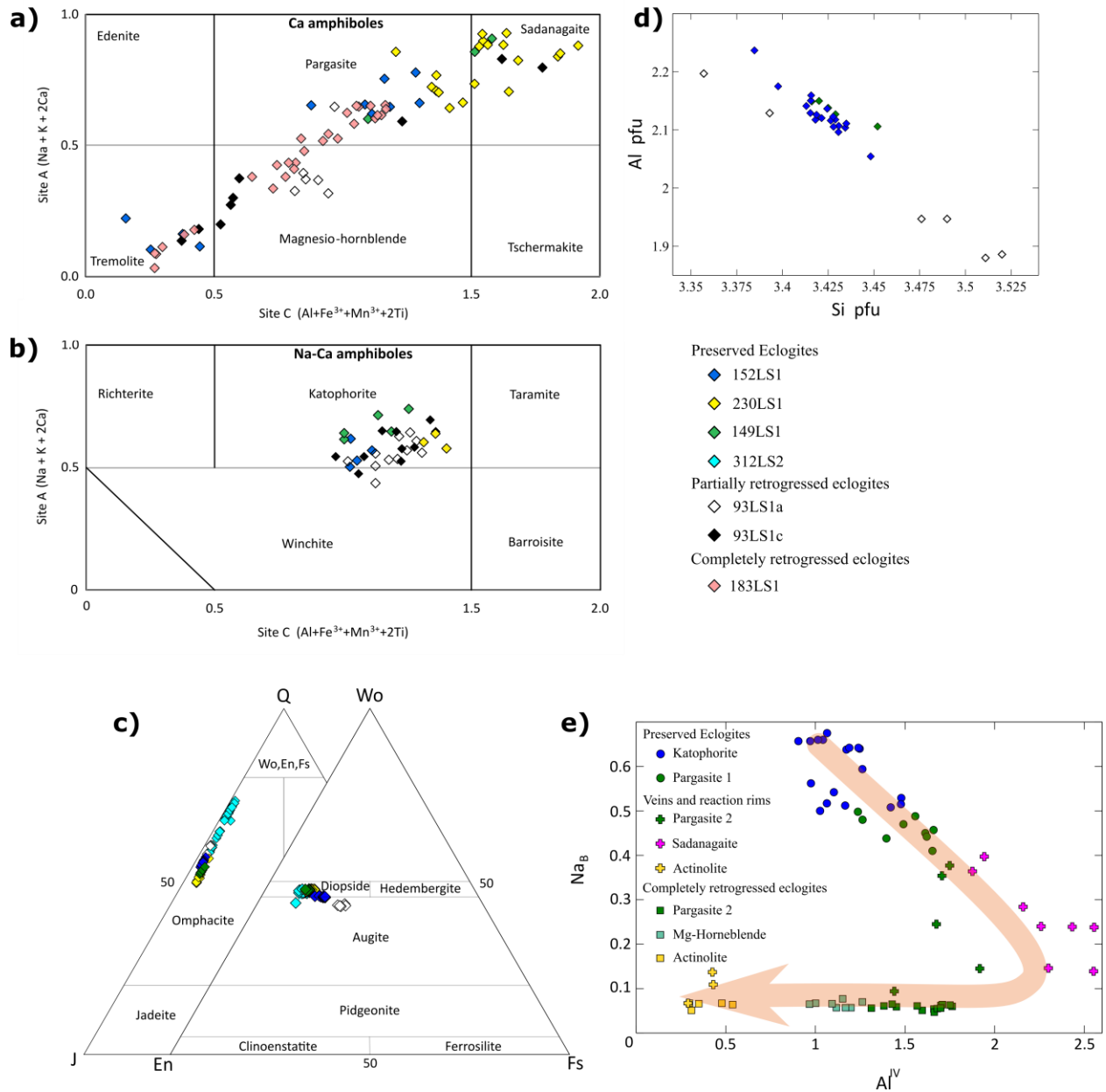


Figure 2.4: **a)** Compositions of calcic amphiboles. **b)** Compositions of calcic–sodic amphiboles (after Hawthorne et al., 2012). **c)** Ternary classification diagram for pyroxenes composition in the Enstatite–Wollastonite–Ferrosilite diagram (foreground), and for sodic clinopyroxenes in the Q–J–A diagram (background) (after Morimoto, 1988). **d)** Phengite compositions in samples 152LS1, 93LS1a and 149LS1; **e)** Summary diagram showing the trends of cation variations (Al^{IV} vs. Na_B) in amphiboles from different textural sites in samples of EPMS metabasites.

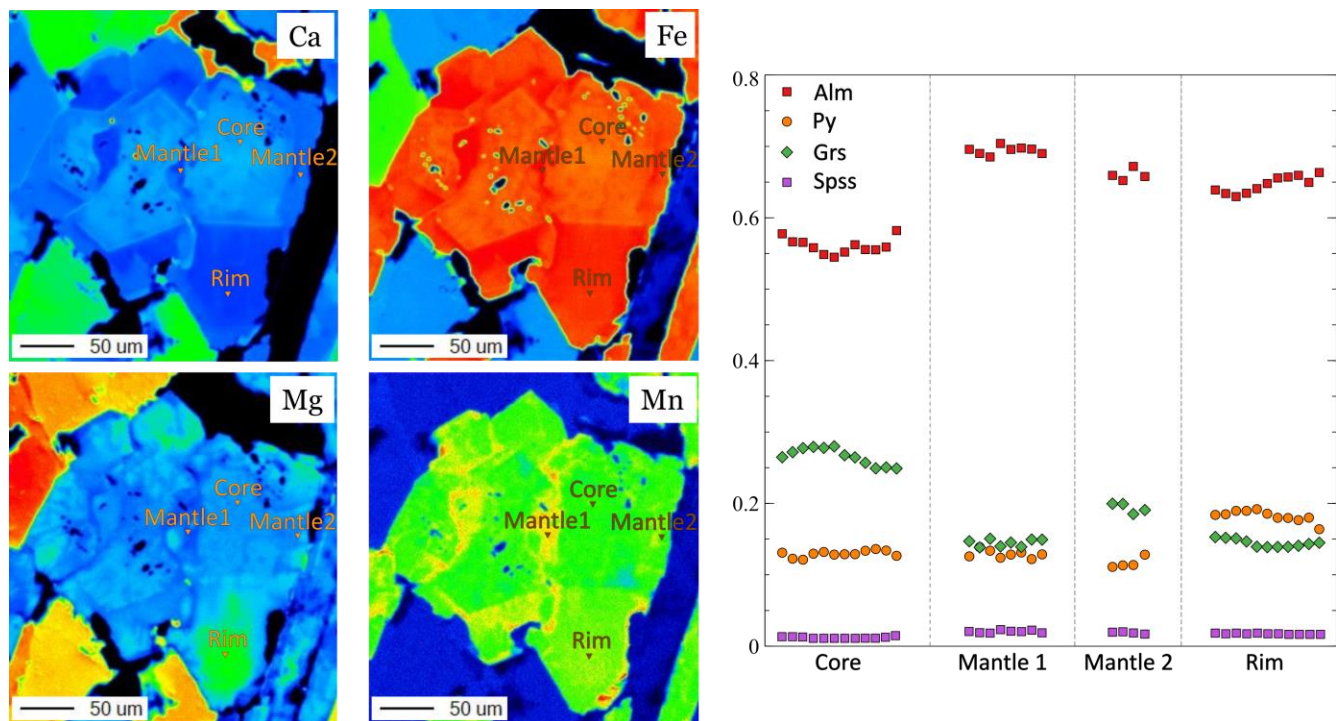
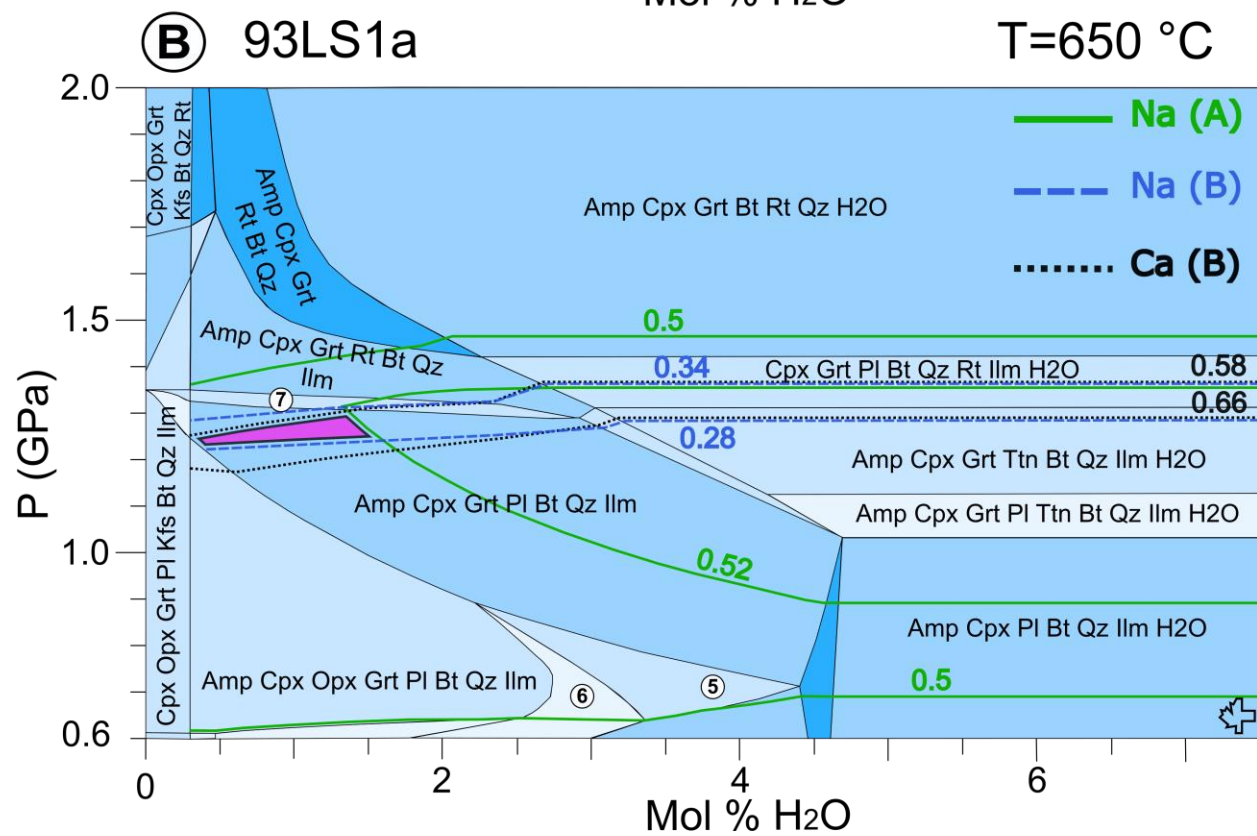
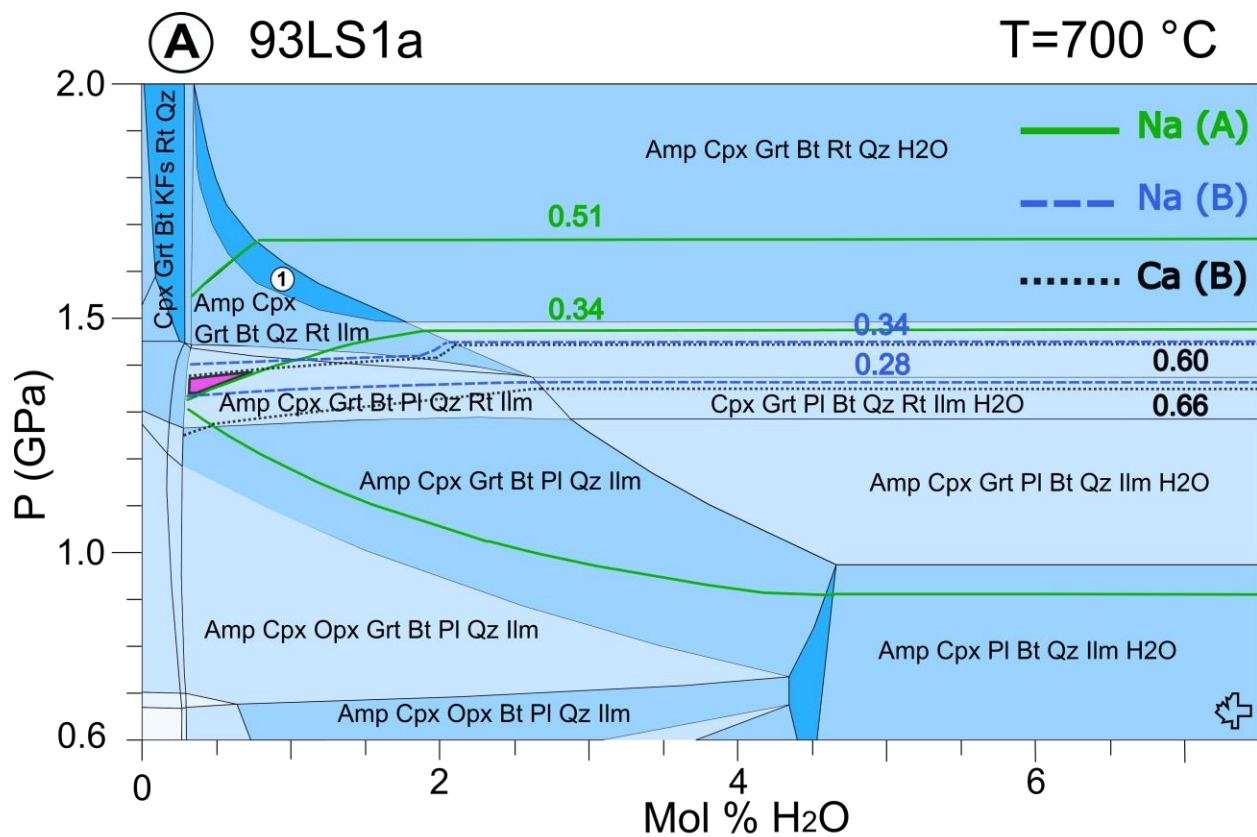


Figure 2.5: Left side: garnet EPMA WDS X-Ray maps of for Ca, Fe, Mg, Mn. Labels indicate the compositional zoning identified within the grain. Right side: EPMA spot analysis compositions representative of the 4 distinct garnet zones identified.



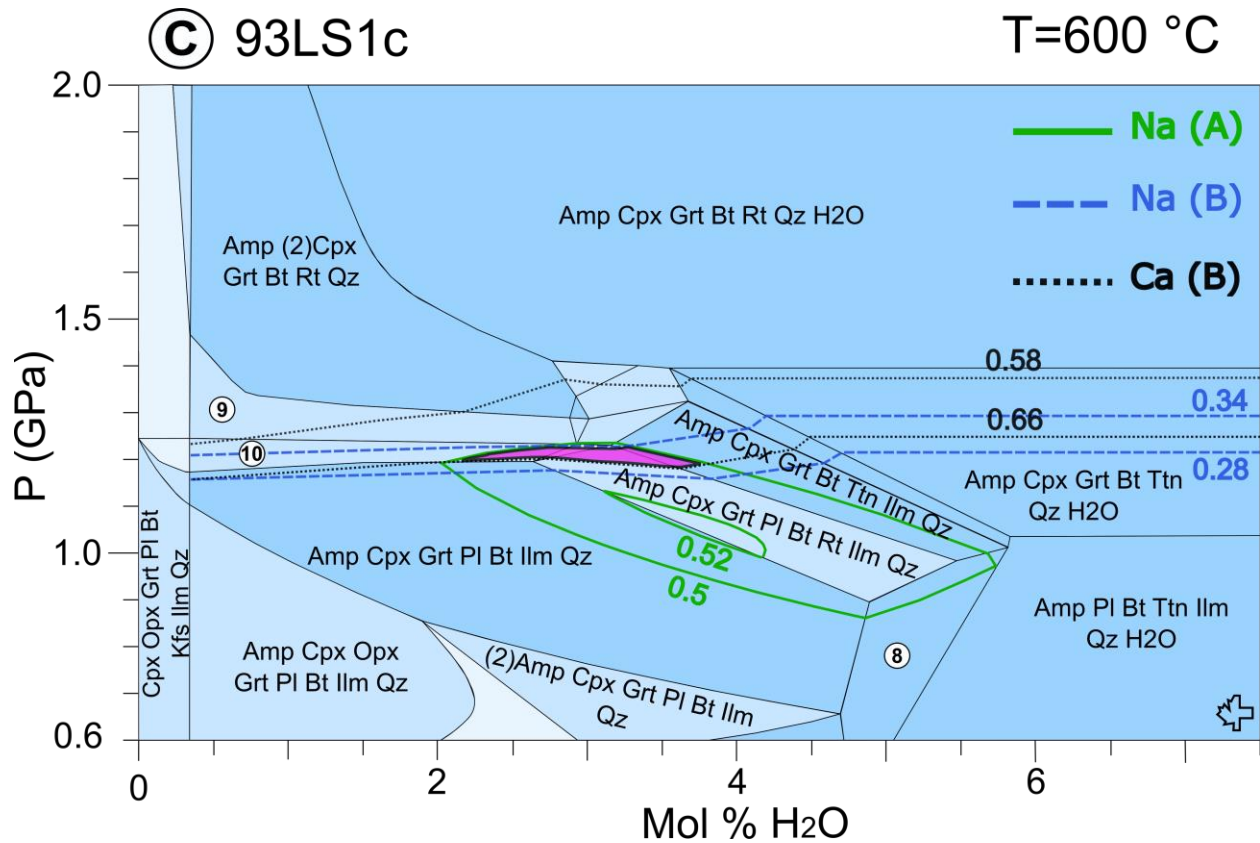


Figure 2.6: P–M(H₂O) pseudosections modelling the earliest stage of eclogite retrograde metamorphism characterized by katothorite growth replacing garnet and omphacite. Pseudosections are calculated at 700, 650 and 600 °C with amphibole isopleths defined by compositional ranges measured with EPMA analyses. Purple fields indicate areas of amphibole isopleth overlap. Some fields are unlabelled for clarity, numbered fields denote the following assemblages: (1) Amp Cpx Grt Bt Qz Rt; (2) Cpx Grt Bt Kfs Qz Rt Ilm; (3) Cpx Grt Pl Bt Qz Rt Ilm; (4) Amp Cpx Pl Bt Qz Ilm; (5) Amp Cpx Grt Pl Bt Qz Ilm; (6) Amp Cpx Opx Grt Pl Bt Qz Ilm; (7) Amp Cpx Grt Pl Bt Qz Rt Ilm; (8) Amp Cpx Pl Bt Qz Ttn Ilm; (9) Amp (2)Cpx Grt Bt Qz Rt Ilm; (10) Amp Cpx Grt Pl Bt Rt Ilm Qz.

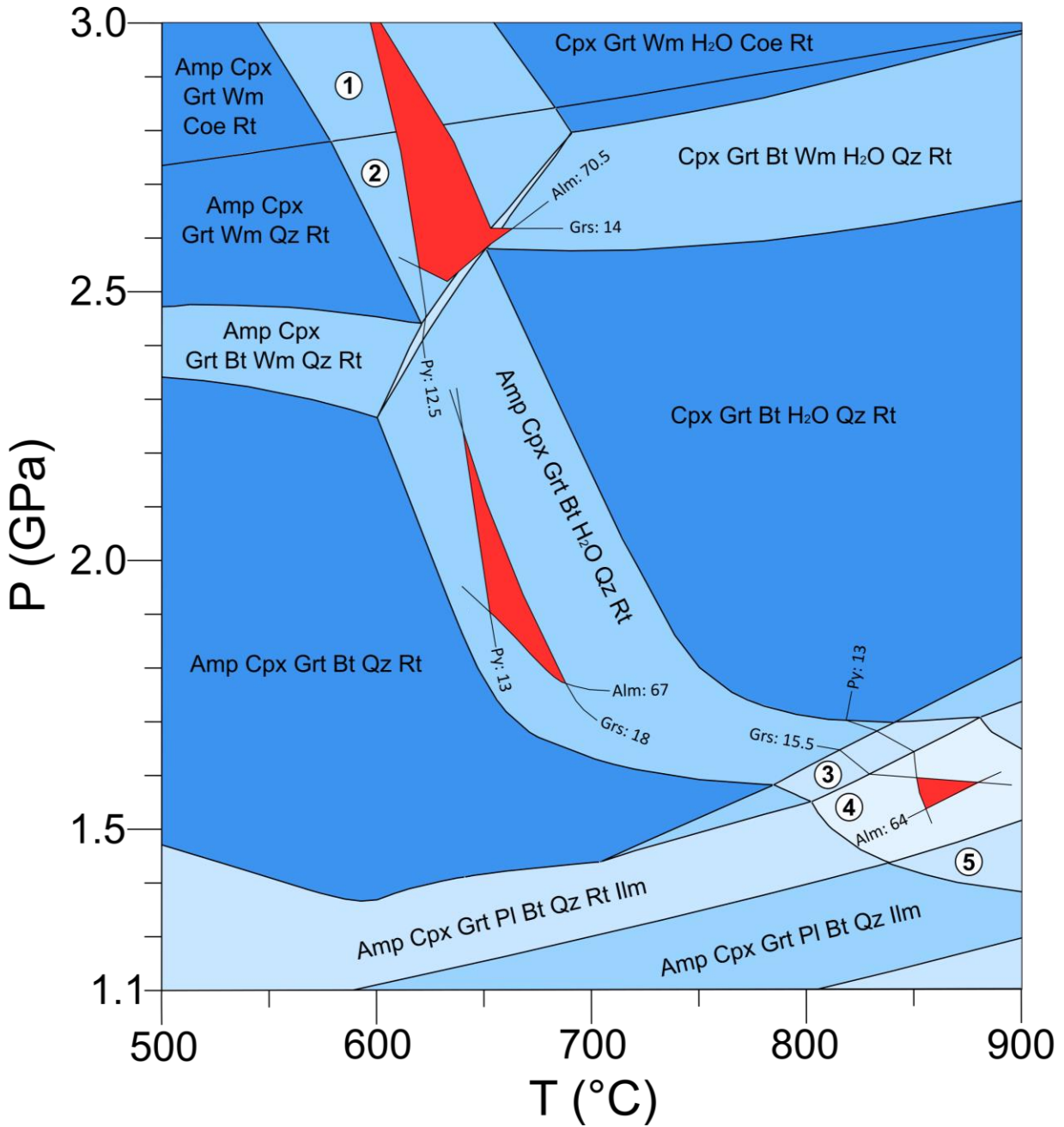


Figure 2.7: P–T pseudosection calculated for the sample of preserved eclogite 93LS1a. The red areas indicate the stability fields of the three metamorphic garnet rims and are defined by contours corresponding to the observed garnet compositions reported in Table A4 – 2. Numbered fields correspond to the following assemblages: (1) Amp Cpx Grt Wm H₂O Coe Rt; (2) Amp Cpx Grt Wm H₂O Qz Rt; (3) Amp Cpx Grt Pl Bt H₂O Qz Rt; (4) Amp Cpx Grt Pl Bt H₂O Qz Rt Ilm (5) Amp Cpx Grt Pl Bt H₂O Qz Ilm.

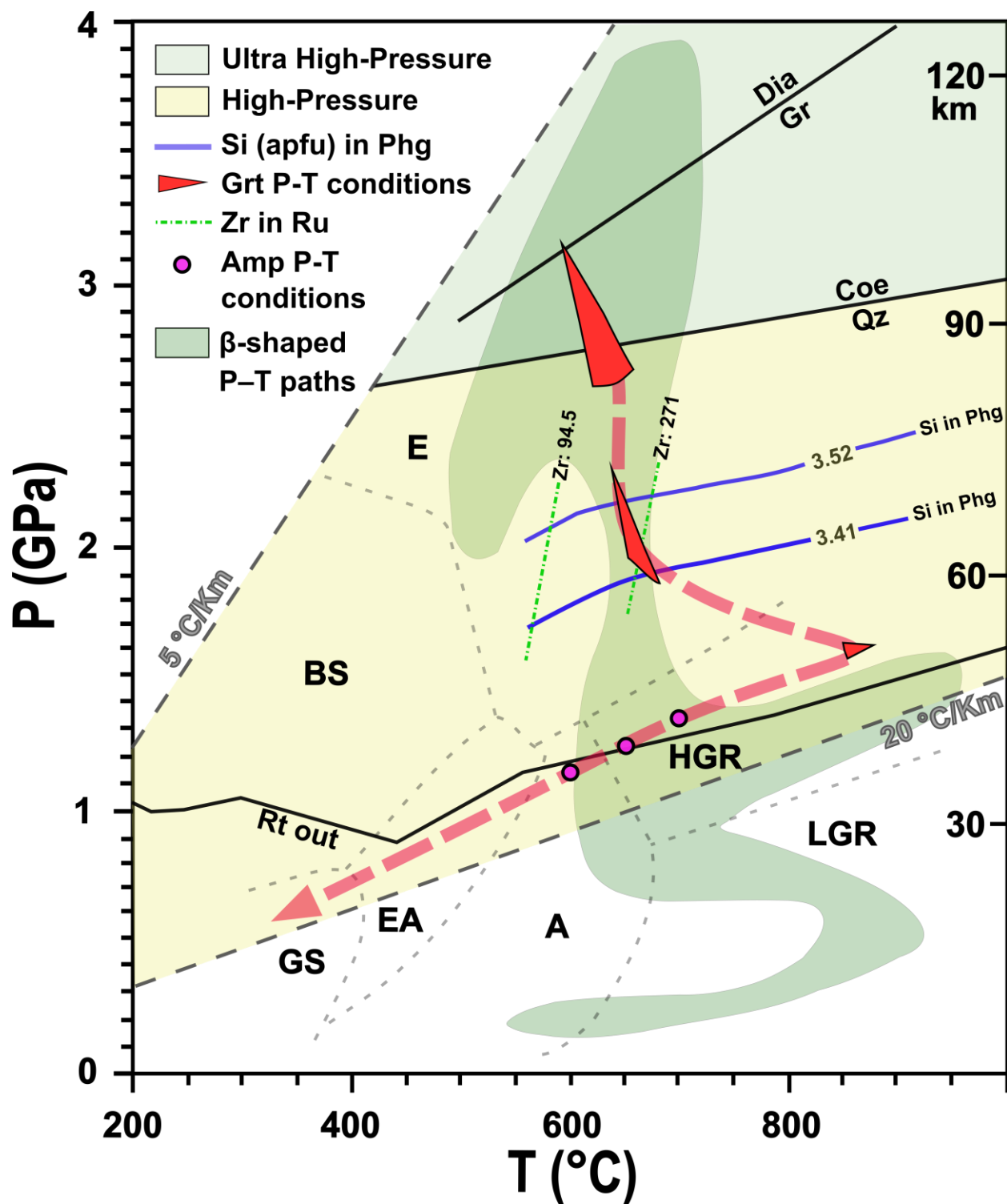


Figure 2.8: P–T diagram summarizing peak pressure and decompression history of East Pond Metamorphic Suite eclogites, constrained by microstructural analysis, compositional isopleth thermobarometry, Zr-in-rutile thermometry and Si-in-phengite barometry. Pressure peak is

reached at the boundary between HP and UHP conditions, then, a first stage of isothermal decompression is followed by decompression associated with substantial heating, defining a β -shaped P–T path. The final segment of the retrograde path, following the T peak, involves katochlorite growth (solid circles), followed by an amphibolite facies assemblage, and culminates in a greenschist facies assemblage. The shaded green field is provided for comparison with other β -shape P–T–t paths from the literature, modified from Fig. 12 of Sizova et al. (2019). Metamorphic facies modified from Liou et al. (1998).

Chapter 3: Petrochronology of the East Pond Metamorphic Suite, Baie Verte Peninsula, Newfoundland

Summary:

The East Pond Metamorphic Suite in the Baie Verte Peninsula, Newfoundland, Canada, provides a unique record of tectono-metamorphic processes during the Middle Ordovician Taconic orogeny. This study utilizes petrochronology to investigate the complex evolution of the East Pond Metamorphic Suite, revealing new insights into the subduction and exhumation history of parts of the Early Paleozoic Laurentian margin. U–Pb geochronology of zircon, rutile, titanite, and apatite—integrated with trace element data—constrain the timing and conditions of metamorphism. We document Late Taconic magmatism on the Laurentian margin, indicated by zircon U–Pb dates from pegmatite intrusions crosscutting the eclogite boudins at c. 443 Ma. These metamorphic rocks exhibit a multi-stage metamorphic history with high-pressure eclogite facies conditions at c. 483–475 Ma, followed by retrograde amphibolite facies overprinting during the protracted deformation. Subsequent stages of exhumation and cooling are recorded by titanite and apatite at ~ 459 Ma and ~452 Ma, respectively. Evidence of the thermal perturbation that resulted in partial melting and pegmatite intrusions suggests that the exhumation of the East Pond Metamorphic Suite was promoted by buoyancy-driven mechanisms triggered by slab break-off. We establish a new chronological framework providing valuable insights into the tectono-metamorphic evolution of the Laurentian margin and the Notre Dame Arc during the Middle Ordovician Taconic Orogeny. Additionally, we link tectonic and magmatic events during subduction and collision highlighting the complex interplay between these processes at different

crustal levels. This approach provides valuable insights into the dynamic interactions that control the tectono-magmatic evolution of collisional orogens.

3.1 Introduction

The Baie Verte Peninsula of the Newfoundland, Canada, Appalachians represents an extraordinary geological setting to study tectono-metamorphic processes associated with subduction and exhumation due to the preservation of variously retrograded eclogitic units formed during the Early to Middle Ordovician Taconic orogeny (Neale et al., 1967; Church, 1969; de Wit and Strong, 1975; Hibbard 1983; Castonguay et al., 2014). Understanding the geologic evolution of the Taconic orogenic cycle is hampered by structural and metamorphic overprinting by younger tectonic events, such as the Silurian Salinic orogeny, and the Early to Late Devonian Acadian and Neoacadian orogenic cycles (de Wit and Strong, 1980, 2014; Jamieson, 1990; Skulski et al., 2010; Willner et al., 2022).

Radiometric dating of metamorphic minerals in poly-deformed orogenic belts characterized by widespread, but heterogeneous metamorphic and structural overprinting, is challenging (e.g., Villa, 2004). Many previous studies have attempted to combine U–Pb geochronology with trace element analysis of accessory phases (e.g., Chen et al., 2010; Corfu et al., 2014; Manzotti et al., 2018; Rebay et al., 2018; Rubatto and Hermann, 2007; Rubatto, 2002; Schmitt et al., 2018), or to use several complementary geochronometers and isotopic systems, including U–Pb in apatite, rutile, titanite, zircon, monazite, allanite, and Lu-Hf and Sm-Nd in garnet (e.g., Anczkiewicz et al., 2012; Butler et al., 2018; Castonguay et al., 2014; Cheng et al., 2018; Engi et al., 2011; Jaranowski et al., 2023; Lotout et al., 2020; Regis et al., 2014; Manzotti et al., 2018; Warren et al., 2012) in high-pressure terrains worldwide to constrain subduction-related metamorphism and the subsequent exhumation history. Careful petrological and trace element analyses were successful

in linking the dates obtained with the metamorphic history allowing the reconstruction of P–T paths in several locations (e.g., Bosse and Villa, 2019; Feng et al., 2024; Roda et al., 2023; Spalla et al., 2011; Walczak et al., 2017; Whitehouse and Platt, 2003, Zucali and Spalla, 2011). However, this approach has not been applied to the variably retrogressed eclogites in the Baie Verte Peninsula that are crucial links between the early and late history of Appalachian orogenesis.

In this work, we combine geochronological data from fresh eclogite occurrences, and eclogites that preserved various stages of amphibolite facies retrograde overprinting, to establish a link between U–Pb dates and the main tectono-metamorphic events related to Appalachian orogenesis and eclogite exhumation. New petrochronological data are presented, which provide constraints on the geologic evolution of the Taconic Orogen, with implications for understanding the tectonic mechanisms related to the exhumation of the deeply subducted Early Paleozoic Laurentian margin. Additionally, we present a case study that illustrates the possibility of linking tectonic and magmatic events in complex orogenic systems.

3.2 Regional Geology

The Newfoundland segment of the Appalachian mountain chain (Fig. 3.1a) includes a complex tectonic collage of oceanic supra-subduction zones and microcontinental terranes, which were accreted to Laurentia throughout its Paleozoic evolution. During this period, which encompasses the closure of the Rheic and Iapetus oceans, the Laurentian margin of the Appalachians progressively expanded oceanwards due to the docking of terranes that had either Laurentian or Gondwanan provenance (Wilson 1966; Nance et al. 2008; van Staal et al. 1998, 2009; Hibbard et al. 2010).

The exotic terrane accretion of the Cambrian-Ordovician Laurentian margin, which in Newfoundland are today referred to as the Humber and Baie Verte margins (van Staal and

Zagorevski, 2020), was episodic, and different tectonic cycles are now identified within the Northern Appalachians; the Taconic, Salinic, Acadian, Neoacadian, and Alleghanian orogenic cycles (Hibbard et al., 2007; van Staal and Barr, 2012).

During the Taconic orogenic cycle, the arc–continent collision between the more inboard segment of the Laurentian margin and the Notre Dame Arc was preceded by the closure of the Taconic seaway, which was driven by the subduction of the outboard segments of Laurentia’s hyperextended continental margin underlain by transitional oceanic crust and mantle and led to the obduction of the Baie Verte oceanic tract (East of the Baie Verte–Brompton Line [BVBL], Fig. 3.1) ophiolites onto the Laurentian margin (van Staal et al., 2007, 2013; Zagorevski et al., 2008, 2023; Skulski et al. 2010). During the Salinic orogenic cycle (440–423 Ma), the Gander margin of Ganderia was accreted to composite Laurentia (van Staal 1994; van Staal et al. 1998, Valverde-Vaquero et al. 2006). The deformation related to the Salinic Orogeny was extensive and strongly overprinted rocks located as far west as parts of the Humber margin (Cawood et al. 1994; Castonguay and Tremblay 2003). The diachronous Acadian orogenic cycle (~ 421–390 Ma) commenced following the Silurian closure of the Acadian seaway and culminated with the collision of Avalonia with composite Laurentia (van Staal 2021a, 2021b).

The study area in the present study comprises the Baie Verte margin, which is principally exposed in part of the Baie Verte Peninsula of northwestern Newfoundland. The rocks of the Baie Verte Peninsula record a complex series of tectono-metamorphic events that are crucial to unraveling the geologic history of the Early to Middle Ordovician Taconic Orogeny in Newfoundland. The Baie Verte margin mainly comprises the Neoproterozoic to Early Paleozoic rocks of a hyperextended continental margin which were partially subducted and exhumed during the Taconic orogenic cycle (van Staal et al., 2013, Castonguay et al., 2014).

The principal regional structure in the Baie Verte Peninsula is the BVBL (Williams and St. Julien, 1981), which marks the Taconic suture between the Baie Verte margin and adjacent supra-subduction zone ophiolitic units of the Baie Verte Oceanic Tract (BVOT) and associated arc terranes (e.g., Notre Dame Arc) (Hibbard, 1983; Skulski et al. 2010; van Staal et al., 2013). The BVBL is a complex shear zone that was tectonically re-activated during subsequent orogenic cycles (Brem et al., 2007; Willner et al., 2022).

The Baie Verte margin comprises basement rocks of the East Pond Metamorphic Suite (EPMS) and structurally overlying Neoproterozoic to Early Ordovician volcanic and sedimentary rocks of the Fleur de Lys Supergroup. The latter includes the Birchy Complex and the Rattling Brook Group (Hibbard 1983), which are interpreted to represent allochthonous parts of the more outboard hyperextended Laurentian margin (van Staal et al., 2013). The EPMS is exposed in an array of structural inliers that contain Pinwarian migmatite, paragneiss, and orthogneiss overprinted by Grenvillian and Taconic metamorphism, overlain by Tonian (~ 950 Ma) volcanic and metasedimentary rocks (de Wit 1980; Hibbard 1983; de Wit and Armstrong 2014; Stowbridge et al., 2022).

3.3 Tectonometamorphic Evolution and Previous Geochronology

Prior to the Taconic orogenic cycle, the Baie Verte margin recorded a 952 Ma bimodal volcano-sedimentary sequence, with the mafic volcanics interpreted as the protolith of the EPMS mafic eclogites. Late Ediacaran rifting is documented by the emplacement of rift-related gabbro and tuffaceous schists between ~564–558 Ma. This was followed by protracted Cambrian crustal hyperextension until ~510 Ma, as suggested by evidence for mantle exhumation in the Birchy complex (Fig. 3.1) and the formation of extensional allochthons, such as the Rattling Brook Group (Fig. 3.1) (Castonguay et al., 2010; van Staal et al., 2013). The earliest recorded Taconic event

involving the Baie Verte margin is represented by the obduction of ophiolitic rocks of the BVOT onto rocks of the Baie Verte margin, located to the west of the Baie Verte Line (Fig. 3.1), which occurred between ~ 485 Ma and ~ 479 Ma based on the age relationships between the BVOT and its unconformable sedimentary cover (Skulski et al. 2010, van Staal et al., 2013). The timing of ophiolite obduction is consistent with a $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende date of 481 ± 6.1 Ma (2 sigma) (Castonguay et al., 2014), obtained from a mafic schist near the structural base of a slice of gabbro imbricated with ultramafic rocks of the BVOT. A metamorphic zircon rim that yielded a U–Pb date of 483 ± 8 Ma (1 sigma) in the EPMS indicates that also the underthrust rocks of the Baie Verte margin record tectono-metamorphism at this time (de Wit and Armstrong, 2014). These age constraints suggest that the underthrusting of parts of the hyperextended Baie Verte margin started at ~ 485 Ma (Castonguay et al, 2014).

The results from previous metamorphic studies suggest that parts of the Baie Verte margin were deeply subducted beneath the BVOT and Notre Dame Arc during the Taconic arc-continent collision. In particular, the existing thermobarometric estimates from metabasites and metasediments of the EPMS constrain the eclogite facies metamorphic peak at 0.7–1.2 GPa (Jamieson, 1990), 1.8–2.0 GPa (Willner et al. 2012), 1.8–1.9 GPa at $\sim 575^\circ\text{C}$ (Massonne, 2024). A U–Pb zircon date of 465 ± 12 Ma (2 sigma) obtained from a partially amphibolitized eclogite of the EPMS provides a minimum constraint on the onset of the Taconic arc-continent collision (Castonguay et al., 2014). This date is interpreted to mark eclogite retrogression and development of the amphibolite facies retrograde metamorphic assemblage. These dates align with those obtained from the Birchy Complex using other chronometers: 466 ± 7 and 460 ± 14 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$, amphibole) (2 sigma); 467 ± 2 Ma ($^{40}\text{Ar}/^{39}\text{Ar}$, white mica) (2 sigma) (Castonguay et al., 2014). The close similarity of the amphibole and white mica dates suggests rapid exhumation of the

Birchy Complex taking into account their different closure temperatures. The final stages of the Taconic collision are characterized by syntectonic magmatism in the Notre Dame Arc between 464 and 459 Ma induced by slab break-off (van Staal et al., 2007).

The two age associations described above (485–479 Ma and 467–460 Ma), are grouped into the oldest deformation event (D_{1-2}), which comprises several generations of folds and cleavages in rocks of the Baie Verte margin, associated with subduction and exhumation of the Baie Verte margin during the Taconic Orogeny (Hibbard 1983; van Staal et al., 2007). Structures related to D_{1-2} are commonly best preserved in the hinges of upright NNE-trending folds formed during D_3 (or D_2 of Castonguay et al. 2014) and are generally transposed into near parallelism with the axial plane foliation (S_3) on the limbs.

The youngest age group related to the Taconic Orogeny is Late Ordovician and was constrained by $^{40}\text{Ar}/^{39}\text{Ar}$ mica dates of 453 ± 1 and 449 ± 12 Ma (2 sigma) obtained from Birchy Complex metapelitic samples (Willner et al., 2022), and by $^{40}\text{Ar}/^{39}\text{Ar}$ amphibole dates of 453.5 ± 8.6 Ma and 440 ± 3.4 Ma from a coarse-grained Advocate Complex gabbro in the town of Baie Verte and from an amphibolite in the EPMS, respectively (Castonguay et al., 2014). These dates are interpreted to be related to the protracted exhumation of the EPMS and to the development of amphibolite-facies metamorphic assemblages in polyphase deformed schistose rocks that formed before the 440 Ma hornblende $^{40}\text{Ar}/^{39}\text{Ar}$ date (Castonguay et al., 2014).

D_3 deformation is associated with greenschist- to amphibolite-facies metamorphism and formed a steep, NE–SW trending foliation (S_3), which is the dominant structure in the Baie Verte margin rocks and the BVOT ophiolites (Skulski et al., 2015). $^{40}\text{Ar}/^{39}\text{Ar}$ mica and amphibole thermochronology constrain D_3 to between 439 and 425 Ma. Further constraints on the timing of D_3 are provided by syntectonic plutons of the Wild Cove suite, late-kinematic Trap Pond pluton,

and migmatite derived from the Fleur de Lys Supergroup which yielded 428 ± 2 Ma, 423 ± 2 Ma, and 428 ± 2 Ma U–Pb monazite dates, respectively (Cawood and Dunning, 1993; Castonguay et al., 2010, 2014; Skulski et al., 2017, Willner et al., 2022; Dallmeyer, 1977).

The latest deformation events—D₄ and D₅—generated fabrics that are commonly well developed near the BVBL and include steeply plunging chevron folds (F₄) with dextral kinematics (Hibbard, 1983; Anderson et al., 2001; Neale and Kennedy, 1967; Goodwin and Williams, 1996). Skulski et al. (2015) interpreted D₄ and D₅ to be related to local amphibolite-facies metamorphism that occurred in the Devonian, which is supported by 358 Ma $^{40}\text{Ar}/^{39}\text{Ar}$ muscovite and 405 Ma (2 sigma) $^{40}\text{Ar}/^{39}\text{Ar}$ hornblende dates. The significance of a Devonian overprinting is supported also by white mica Rb/Sr date of 356 ± 5 Ma (2 sigma) (Willner et al., 2022) obtained from a phyllonite sample overprinting D₁–D₂ fabrics. On the W side of the BVBL, Devonian $^{40}\text{Ar}/^{39}\text{Ar}$ amphibole and mica dates range between 419 and 384 (Dallmeyer 1977; recalculated by Skulski et al., 2017 with revised decay constants and internal standard ages).

Previous geochronology and thermochronology results highlight the intricate geological evolution of the Baie Verte Peninsula, characterized by a complex tectonic and geochronologic record formed over several orogenic cycles that occurred between the Early Ordovician and the Devonian. Despite the prolonged overprint, the EPMS eclogitic mafic rocks and their metasedimentary hosts still preserve structures and metamorphic assemblages associated with the oldest phases of subduction and exhumation during the Ordovician Taconic Orogeny. We focus in the present study on the timing of the Taconic burial and exhumation of the Laurentian margin rocks using U–Pb geochronology of metabasites, metasediments, and magmatic rock samples of the EPMS.

3.4 Petrography and Accessory Mineral Imaging

More than 150 mafic boudin samples were collected during this study and subject to detailed petrographic analysis. The five samples selected in this work preserve the most important metamorphic and deformation events that allow the reconstruction of the evolution of the East Pond Metamorphic Suite eclogites (Fig. 3.1). Polished thin sections were used for transmitted and reflected light microscopy. Separation of mineral fractions (rutile, apatite, titanite, and zircon) was done at Memorial University (MUN), Canada using a combination of crushing, sieving, panning, and heavy liquid techniques. Grains were hand-picked, mounted in epoxy resin, and polished to reveal the crystal interiors. Cathodoluminescence (CL) imaging for zircon and apatite, and back-scattered electron (BSE) imaging for rutile and titanite were done using a JEOL JSM 7100F Field Emission Gun Scanning Electron Microscope (FEG-SEM) at MUN to characterize the internal structure(s), morphology, and mineral inclusions. Minerals were identified using energy-dispersive spectroscopy (EDS) at 15 kV and 50 nA. The epoxy mounts and thin sections were used for subsequent investigations using both Electron Probe Microanalysis (EPMA) and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS).

3.5 Mineral Compositions

Mineral compositions were determined using a JEOL JXA-8230 SuperProbe electron probe microanalyzer at The Earth Resources and Analysis (TERRA) Facility at MUN. EPMA analyses of rutile, apatite, and titanite, were used as internal standards to convert counts to concentration in the LA-ICPMS trace element analyses. Detailed information about the EPMA analytical conditions and the synthetic and natural standards used are summarized in the Table A1 - I. Major and minor element concentrations of rutile, apatite, and titanite are reported. Rutile was analyzed for Ti, Fe, Nb, Zr, Ca, Mg, Al, and Cr. Apatite was analyzed for F, P, Cl, and Ca. Titanite was

analyzed for Si, Ca, Ti, Fe, and Al. EPMA analyses were done as close as possible to the craters where the LA-ICP-MS analyses were previously done. Raw X-ray intensities were corrected using JEOL software using standard ZAF techniques.

3.6 U-Pb and Trace Element Petrochronology

Uranium-Pb isotope and trace element analyses were done at the Micro Analysis Facility (MAF) at MUN using a Thermo-Finnigan Element XR ICP-MS in combination with a Geolas 193 nm ArF Excimer laser. Helium gas with a flow rate of 1.25 l/min was used to transport the ablated material, with N₂ added to the Ar carrier gas for increased sensitivity and additional Ar make-up gas added after the ablation cell before injection into the ICP-MS. After collecting a background for 30 seconds, the samples were ablated for 60 seconds. Apatite, titanite, and zircon were analyzed from mineral separates, while rutile was analyzed both in situ and from mineral separates that yielded the same results. U-Pb isotope and trace element analyses were collected simultaneously (Tables A5).

3.6.1 Zircon U-Pb Analyses

Zircon grains from granitoid pegmatite sample 205LS1 were analyzed using a laser spot size of 30 µm at a repetition rate of 5 Hz and a laser fluence of 4.0 J/cm². Zircon reference material 91500 (1062 Ma, Wiedenbeck et al., 1995) and Plešovice (337 ± 1, Slama et al., 2008) were used as primary reference materials, and 02123 (295±1 Ma, Ketchum et al., 2001) was used as secondary reference material.

3.6.2 Rutile U-Pb Analyses

Rutile separates from samples 152LS1 (both in-situ and from separates), 93LS1, and 230LS1 were analyzed using a laser spot size of 40 µm at a repetition rate of 5 Hz and a laser fluence of 4.0 J/cm². Primary rutile U–Pb reference materials used were R10 (1091.3 ± 4.7 Ma, Luvizotto et al.,

2009) and R-632 (496 ± 2 Ma, Axelsson et al., 2018). RMJG (1750.6 ± 8.4 Ma, Zhang et al., 2020) and PCA (1865 ± 8 Ma, Bracciali et al. 2013) were used as secondary reference materials.

3.6.3 Titanite Analyses

Titanite grains from samples 93LS1c and 183LS1 were analyzed using a laser spot size of 40 μm at a repetition rate of 10 Hz and a laser fluence of 4.0 J/cm². Primary and secondary titanite U-Pb reference materials were the Tory Hill titanite (1039 ± 23 Ma, Fisher et al., 2020) and the Kuehl Lake titanite (in-house secondary standard, 1062 Ma).

3.6.4 Apatite Analysis

Apatite grains from sample 183LS1 were analyzed using a laser spot size of 40 μm diameter, at a repetition rate of 10 Hz and a laser fluence of 4.0 J/cm². Tory Hill apatite (1021 ± 3 Ma, Fisher et al., 2020) was used as the primary reference material. Erongo (134.49 ± 0.61 Ma, Amelin and Zaitsev, 2002) and Ipirá (inferred from zircon ages ranging from 2082 and 2072 Ma, de Sousa et al., 2020) apatite were used as secondary reference materials.

3.6.5 Trace Element Analysis

For every mineral analyzed, the primary reference material for trace element analysis was NIST 610 with BCR-2G used as the secondary reference material. EPMA analyses were used as an internal standard to normalize the intensity of trace elements, in particular, Ti was used as the internal standard for rutile and titanite, and Ca for apatite. Iolite software v.3 (Paton et al., 2010; 2011) was used for all U-Pb and trace element data reduction. For U-Pb geochronology, we used an exponential-linear down-hole U-Pb fractionation correction model. Isoplot 3.7 (Ludwig, 2003) was used for age calculations, and the age uncertainties are reported at the 2 sigma (95%) confidence level.

3.7 Field Relationships

Mafic rocks of the EPMS form foliation-parallel boudins enveloped by metasedimentary host rocks (Fig. 3.2A). Although the boudins are most commonly amphibolites (e.g., sample 183LS1), the eclogite assemblage is locally preserved in their cores (e.g., samples 93LS1, 152LS1, 230LS1). Eclogite boudins show a gradual increase in the degree of amphibolitization from interior to rim, where they can be completely replaced by amphibolite-facies assemblages (Fig. 3.2A). The protolith of the amphibolite boudins in the EPMS are considered to be eclogites based on their similar trace element compositions (Massonne et al., 2022). In the boudin cores, a continuous S2 eclogitic foliation is marked by a shape-preferred orientation of omphacite, phengite, rutile, and quartz ribbons (Fig. 3.3A). In the amphibolitized eclogite rims, S2 is marked by a shape-preferred orientation of amphibole and quartz (Fig. 3.3C). Blue-green amphibole is parallel to S2, which indicates that D2 represents a progressive deformation event that developed under metamorphic conditions different from the eclogite facies. The mafic boudins and the metasediments are folded by upright, tight to isoclinal F3 folds, which is the dominant regional structure.

Pegmatitic dikes crosscut the eclogite–amphibolite boudins (Fig. 3.2B). These dikes intersect the internal eclogitic to amphibolitic foliation at a high angle, indicating that their intrusion occurred after the onset of amphibolitization of the boudins, hence after or late-during D₂. Amphibole-rich coronitic rims locally developed in the mafic boudins where in contact with the pegmatites, suggesting continuous development of amphibolite facies conditions in the mafic rocks during this magmatic event. Granitic leucosome, locally garnet-bearing, derived by in-situ partial melting, are found in the mafic boudins and their metasedimentary host rocks (Fig. 3.2C). However, the relationships between leucosome and pegmatite could not be univocally defined in the field.

3.8 Sample Descriptions

Eclogite sample 152LS1 exhibits a well-developed foliation (S₂) (Fig. 3.3A), characterized by the preferred orientation of omphacite, phengite, quartz, rutile aggregates, and poikiloblasts of blue-green amphibole-1. Garnet in the matrix is idioblastic to sub-idioblastic and contains 5–30 µm inclusions of quartz, amphibole, and rutile. Garnet and omphacite are xenoblastic where included in blue-green amphibole-1 poikiloblasts. The well-preserved eclogite facies assemblage is crosscut by a network of 0.5–2 mm wide veins rich in green amphibole. In the veins, a titanite rim envelops rutile; amphibole and plagioclase symplectite replace omphacite and green amphibole rims locally envelop blue-green amphibole-1 cores. A 2-5 mm-wide reaction rim surrounding the veins is indicated by symplectite at omphacite grain boundaries. Rare individual subhedral grains of apatite, occur in the matrix and can be aligned with or at a high angle to S₂.

Eclogite sample 93LS1 comprises a S₂ foliation marked by the preferred orientation of blue-green amphibole-1 and quartz (Fig. 3.3C). Fractured garnet porphyroblasts are xenoblastic and are enveloped by epidote rims. Omphacite is locally preserved and is surrounded by symplectite of amphibole and plagioclase. Rutile is present in the matrix or as inclusions in the blue-green amphibole; often exhibiting rims of titanite (Fig. 3.3C). White mica is surrounded by biotite and plagioclase symplectite. The matrix is composed of symplectitic intergrowths of secondary amphibole, plagioclase, biotite, and aggregates of titanite and calcite with elongation parallel to S₂. Apatite occurs as sub-idioblastic grains included in quartz.

Samples 230LS1, 183LS1, and 205LS1, described below, were collected from different outcrops in the same locality.

Eclogite sample 230LS1 comprises porphyroblasts of garnet and omphacite, in a weakly foliated matrix of quartz, amphibole-1, rutile, and clinozoisite (Fig. 3.3B). Garnet forms irregular

grains including quartz, rutile, clinozoisite, omphacite, and amphibole. Omphacite grains have rutile inclusions. Symplectitic intergrowths of amphibole and plagioclase are observed at the omphacite grain boundaries. Clinozoisite grows especially where the green-blue amphibole-1 is present, and at their contact, there are biotite–quartz–plagioclase symplectites.

Amphibolite sample 183LS1 has a coronitic texture with xenoblastic porphyroblasts of amphibole-1 including titanite, epidote, and biotite (Fig. 3.3D). The unfoliated matrix consists of intergrowths of lath-shaped green amphibole 2, and fine grain aggregates of plagioclase, quartz, and K-feldspar. Titanite, epidote, and apatite in the matrix are sub-idioblastic to xenoblastic.

Pegmatite sample 205LS1 has granoblastic texture and crosscuts mafic boudins and their amphibolite-facies foliation (Fig. 3.2B). It consists of plagioclase, quartz, white mica, biotite and rare epidote. The dike contacts with the metasediments and mafic pods are sharp.

3.9 Petrochronology

3.9.1 Zircon

Zircon from pegmatite 205LS1 forms mainly fragmented or subhedral grains with sizes from 20×30 to $150 \times 210 \mu\text{m}$ (Fig. 3.4A). Eighty-four analyses were done for trace element concentrations and U-Pb geochronology. Five distinct age populations have been defined based on concordant U-Pb dates, trace element compositions, and zircon internal zoning and textures.

Several of the analyses yield dates much older than the main population. One zircon grain with a Th/U ratio of 0.4, and a distinct chondrite normalized REE pattern characterized by a positive Ce anomaly and negative Eu anomaly, yielded an inherited discordant date of 1480 ± 43 Ma (Fig. 3.4B). Two zircon grain cores, bright in CL displaying sector and complex internal zoning respectively, have Th/U ratios of 0.64 and 0.42 and are characterized by a positive Ce anomaly, a negative Eu anomaly, and a positively-sloped chondrite normalized HREE pattern; they yielded a

poorly defined concordia age of 957 ± 12 Ma (MSWD: 8.6; < 9% discordant) (Fig. 3.4B). Two analyses from the core and rim of a zoned, subhedral, zircon grain with Th/U ratios of 0.04 and 0.19, and a chondrite normalized REE pattern defining a Ce anomaly and a positively-sloped MREE and HREE pattern yielded concordia age of 618 ± 37 (MSWD: 0.98) (Fig. 3.4B). Finally, two discordant analyses from the core and rim of an elongated, rounded zircon grain yielded imprecise ^{207}Pb corrected dates of 590 ± 59 and 519 ± 77 (outside of diagram boundaries in Figure 4.4B). This zircon shows the most enriched LREE composition of the sample (La: 90 ppm and 125 ppm, respectively). Trace element compositions of concordant zircon populations described above are reported in Table A5 – IV. Three zircon grains define a concordia age of 479 ± 8 Ma (MSWD: 1.4; < 13% discordant) (Fig. 3.4B), these grains have extremely low Th/U ratio (< 0.01), mostly flat chondrite normalized LREE patterns, and a positive-sloped MREE and HREE patterns.

The majority of grains display complex to irregular internal zoning, characterized by dark cores and bright rims in CL (e.g., grain 28, Fig. 3.4A), and less commonly have patches of igneous growth zoning (e.g., grain 56, Fig. 3.4A). Both domains have Th/U ratios <0.03. Rim domains have higher concentrations of LREE and lower concentrations of HREE than core domains (Fig. 4.6C). Regression of cores and rims defines a linear array along a single discordia line in Tera-Wasserburg concordia space. A Model 1 regression (Ludwig, 2003) defines a Late-Ordovician date of 443 ± 2 Ma (MSWD: 7.4; N: 63) (Fig. 3.4D and E). Six outliers were excluded from the regression for marked deviation from the weighted average value (Fig. 3.4C). Regression of core domains yielded lower intercept dates of 451 ± 5 Ma (MSWD: 2.2; N: 12), whereas rim domains yielded slightly younger—but within uncertainty—lower intercept date of 446 ± 4 Ma (MSWD: 2.1; N: 18). In a $(\text{Sm}/\text{La})_{\text{N}}$ vs La diagram (Fig. 3.5), the rim data plot near the hydrothermal region while core data plot nearer to the magmatic region defined by Hoskin (2005). Mean crystallization

temperatures for the two zircon domains were calculated by Ti-in-zircon geothermometry (Watson et al., 2006) at $\sim 840 \pm 80^\circ\text{C}$ for the bright domains and $\sim 930 \pm 80^\circ\text{C}$ for the dark domains. Ti-in-Zr results are reported but not used for tectonic interpretations due to the unknown Ti activities during zircon growth in sample 205LS1.

3.9.2 Rutile

Rutile U-Pb dates for two EPMS eclogites yielded relatively imprecise results due to low U contents, ranging from 1.4 to 4.6 ppm. Rutile analyses characterized by contamination from inclusions and those with large analytical uncertainties were not considered for statistical analysis and regressions. The accepted and discarded data are nonetheless reported for each sample in Table A5 – I.

Rutile from fresh eclogite sample 152LS1 forms aggregates elongated parallel to S₂, it is reddish, anhedral to subhedral, with sizes varying from 40 x 60 to 110 x 190 μm . From a total of 29 analyses, 12 data with discordance >15% were excluded from the regression to avoid introducing the source of error caused by non-systematic common lead contamination. The 17 accepted analyses yielded a concordant age of 483 ± 18 Ma (MSWD: 1.6, discordance < 15%) (Fig. 3.4F).

Rutile from retrogressed eclogite sample 93LS1 forms aggregates elongated parallel to S₂, it is reddish, subhedral to anhedral, and ranging from 40 x 80 to 150 x 230 μm in size. The accepted 51 analyses yielded a concordia age of 499 ± 12 Ma (MSWD: 2) (Fig. 3.4G). The kernel density estimation (KDE) diagram (Fig. 3.4H) indicates the presence of multiple age groups in this sample, particularly at c. 470, 510, 570, and 620 Ma. This supports the hypothesis that 499 ± 12 Ma may represent a mixed age of zircon domains recording slightly different dates rather than a single crystallization event.

Trace element concentrations and U-Pb geochronology of rutile from eclogite sample 230LS1 were done in situ on a polished thin section. The red equant to prismatic rutile grains from this sample varied in size from 250x 520 to 400 x 700 μm . The U content was too low (average U concentration: <0.1 ppm) to yield a meaningful U-Pb date.

Rutile from the three samples analyzed have trace element compositions (Fig. 3.6A) characteristic of metabasic eclogites (Nb < 900 ppm; Cr < 1000 ppm; Zr < 500 ppm; see Table 3 in Zach et al., 2002). An exception is the Zr-content of some rutile grains in 93LS1 that ranged up to 1010 ppm (Table A5 – I), considered diagnostic of rutile formed in mafic granulites (Zach et al., 2002). All the rutile grains analyzed have Sn and W concentrations lower than 200 and 1000 ppm, respectively, consistent with being metamorphic rutile (Agangi et al., 2020).

Zr-in-rutile thermometry was done using the calibration from Tomkins et al. (2007), and yielded temperatures ranging between ~ 525 and 575°C for 152LS1, ~ 525 – 700°C for 93LS1, and ~ 550 – 625°C for 230LS1. The temperature estimates are summarized in Figure 4.7. Application of Tomkins et al. (2007) calibration requires knowledge of the pressure. For the maximum temperature estimate of rutile crystallization (or re-equilibration), we used the peak pressure values of 1.85 GPa obtained for a mafic eclogite of the EPMS estimated by Massonne (2024).

3.9.3 Titanite

Titanite from eclogite with a variable amphibolite facies overprint (sample 93LS1) is subhedral with sizes ranging from 125×200 to 300×450 μm . In total, 92 grains were analyzed for trace element concentrations and U-Pb geochronology and yielded a discordant age of 459 ± 11 Ma (MSWD: 0.78; probability of fit: 0.94) (Fig. 3.4I). The spread in common Pb values allowed for a precise estimate of the initial common Pb composition of the sample through “free regression” (common Pb: 0.881 ± 0.01). Hence, common Pb corrections, such as Stacey and Kramers (1975)

correction, were not necessary. Back-scattered electron images combined with trace element concentrations defined gradational trends, corresponding to titanite core and rim domains. Core domains have lower LREE, MREE, flatter HREE chondrite normalized patterns, and lower U (5.8 ppm average) than rim domains (14.9 ppm average) (Fig. 3.6B). Regression of core domains—dominated by common Pb—results in regression with uncertainties too large to lead to any meaningful geologic interpretation. Rim domains contain more radiogenic Pb; when “anchored” with an initial common Pb value of 0.881 ± 0.01 the rims domain yield a date of 455 ± 21 Ma (MSWD: 0.79; probability of fit: 0.88), which is within the uncertainty of the regression of cores and rims together. Zr-in-titanite thermometry has been applied according to the pressure-dependent calibration from Hayden et al. (2008). The temperature estimate (Fig. 3.7) is in the range of 650–775°C based on a constant pressure of 1 GPa, which is broadly considered to be the upper-pressure limit for titanite stability (e.g., Angiboust and Harlov, 2017). Titanite cores and rims did not show significant differences in the calculated crystallization temperatures.

3.9.4 Apatite

A total of 87 LA-ICPMS measurements were obtained from apatite grains in a completely amphibolitized eclogite near the contact with a pegmatite intrusion (sample 183LS1). The results define a lower intercept date at 452 ± 16 Ma (MSWD = 1.6; probability of fit: 0.0003) (Fig. 3.4L). Apatite chondrite normalized REE element patterns highlight a high variability in LREE (e.g., La: 1–635 ppm), a negative Eu anomaly, and a negatively- to flat-sloped HREE pattern (Fig. 3.6D). Analyses with lower La concentrations have greater Eu anomalies and flatter HREE patterns than the analyses with higher La. Additionally, analyses with lower La generally contain a higher proportion of radiogenic Pb than the other analyses, which contain proportionally more common Pb. Separate regression of the data with low and high La—with variable proportions of radiogenic

to common Pb—did not yield any statistically meaningful result, therefore we treated it as a single dataset. A common lead correction was not necessary because the spread in common Pb values allowed a “free regression” to obtain the common Pb composition (common Pb: 0.8455 ± 0.0055).

3.10 Discussion

3.10.1 Limitations and Assumptions

The EPMS has undergone multiple phases of metamorphic mineral growth from the Mesoproterozoic to the Late Paleozoic. This complex metamorphic evolution hinders straightforward geochronological investigations because the isotopic evolution of the various events may overlap or reset earlier records of growth (Terry and Robinson, 2003; Ague and Baxter, 2007). Additionally, the common occurrence of disequilibrium textures challenges the assumption of chemical equilibrium in metamorphic rocks (e.g., Caddick and Thompson, 2008; White et al., 2008). In the EPMS, such textures suggest that accessory minerals marking superimposed metamorphic assemblages may reflect growth over prolonged and possibly overlapping metamorphic reactions rather than representing discrete metamorphic events (Villa, 2006; Carlson, 2010). We undertook a careful petrologic analysis, on an extensive suite of thin sections, in order to identify the sequence of metamorphic and structural events and to enable a meaningful petrochronologic interpretation.

Correcting for common Pb in accessory minerals such as titanite, rutile, and apatite presents a significant challenge in U-Pb geochronology (Zach et al., 2011). Common Pb, if not properly accounted for, can lead to inaccurate age determinations. This issue is particularly critical for minerals that do not strongly exclude divalent Pb during crystallization or have undergone post-crystallization alteration of the initial isotopic composition (Kohn, 2017; Chew et al., 2014). In this study, we used several strategies to address the problems related to common Pb. First, we

excluded grains or grain domains affected by common Pb identified during careful examination of the data. For example, first, we obtained a rutile concordia age in sample 152LS1 by eliminating the high common Pb discordant data that presented significant scatter and hindered meaningful age determination (Corfu, 2013). Second, we evaluated the applicability of the Stacey-Kramers (1975) model to estimate the initial common Pb composition and applied corrections accordingly. However, in none of the cases was this correction applicable due to: (i) overestimation of the common Pb composition, leading to apparent ages older than those obtained by “free regression”; and (ii) the corrected regression excluded the majority of the data points, thus failing to represent a best-fit line through the data. Third, free regression of the U-Pb isotope data for titanite and apatite yield well-defined intercepts with reasonable common Pb ratios (Chew et al., 2014). Therefore, we argue that a free regression of these datasets (e.g., titanite in sample 93LS1 and apatite in sample 183LS1) provided a relatively accurate age of the sample (Chew et al., 2014; Schoene, 2014; Horstwood et al., 2016). Finally, where possible, we cross-validated dates obtained from different minerals and isotopic systems (e.g., zircon) to corroborate the U-Pb dates and mitigate the uncertainties introduced by common Pb (Corfu, 2013). These methods, and a case-by-case evaluation of possible scenarios, allowed us to address the limitations posed by common Pb and enhance the reliability of our geochronological data.

A significant limitation in petrochronological studies is the decoupling between U-Pb and REE systematics, particularly in accessory minerals such as titanite. This decoupling arises from complex coupled dissolution-reprecipitation reactions, which can alter the original geochemical signatures without completely resetting the U-Pb isotopic system (Hermann and Rubatto, 2003). Addressing this issue requires coupled analysis of trace elements and U-Pb using chemical mapping to define homogeneous domains in each grain (Kohn, 2017). In this study, we aimed to

improve the geochronological framework of the progressive metamorphic evolution of the EPMS eclogites to amphibolite. Hence, we opted to analyze a large number of grains to enhance the statistical robustness of age determinations. Future detailed studies of the systematics of each accessory phase analyzed herein may reduce our large age uncertainties and produce more accurate age constraints.

Zr-in-rutile and Zr-in-titanite thermometry requires Zr-saturated systems; however, in this study, it is applied to Zr-undersaturated samples, introducing a potential source of error in the crystallization temperature estimates. Consequently, the derived temperatures should be considered as minimum estimates. Despite this limitation, we argue that these estimates remain valuable for tracing the thermal evolution of the samples. They provide critical constraints on the relative changes in temperature during the metamorphic history, offering insights into the broader tectonic processes.

3.10.2 Tectonic Implications of the Petrochronological Record

The new petrochronology dataset from the EPMS provides important tectonic constraints on the Baie Verte region and the overall tectonic evolution during the Taconic orogenic cycle. Below, we present the tectonic history chronologically, from the oldest to the youngest events recorded by the accessory minerals in the samples analyzed.

Inherited Zircon Geochronology: Records of Magmatism and Metamorphism Prior to Taconic Subduction and Exhumation

Out of the five zircon populations identified in the pegmatite 205LS1 (Figs. 4B and C) which crosscut the metasedimentary rocks and eclogite boudins, four are interpreted to be inherited, most

likely from the metasedimentary host rocks. Textures and trace element compositions of zircon populations dated at ~1480 Ma, ~957 Ma, and ~618 Ma, suggest these have a magmatic origin. Mesoproterozoic ages have been previously documented in a granitic gneiss of the EPMS basement unit (de Wit and Armstrong, 2014) (Fig. 3.8). Magmatic zircons dated at ~957 Ma are consistent with Tonian ages in volcano-sedimentary sequences of the EPMS (Strowbridge et al., 2023). Dates of 618 Ma are broadly consistent with magmatism associated with the protracted opening of the Iapetus Ocean in Newfoundland (Kamo et al., 1989; Cawood et al. 2001) and the British Isles (Dempster et al., 2002; Fettes et al., 2011). The two remaining zircon populations dated at ~590–519 Ma and ~479 Ma, respectively have REE patterns and Th/U ratios greater than 0.1, which suggest a metamorphic origin (Hoskin and Schaltegger, 2003; Kirkland et al., 2015). The oldest population probably crystallized during deformation and metamorphism associated with prolonged hyperextension of the Laurentian margin (van Staal et al., 2013). The younger population is generally consistent with existing age constraints on early Taconic subduction-related metamorphism (de Wit and Armstrong, 2014; Castonguay et al., 2014) (Fig. 3.8). Hence, we suggest that late-Taconic pegmatites assimilated zircon populations from the metasedimentary host rock, which dates are consistent with the data available on the metamorphic and magmatic evolution of the Baie Verte margin during the Mesoproterozoic and Paleozoic.

Rutile Geochronology—Metamorphic Records of Hyperextension and Subduction

The ~480 Ma date recorded by rutile (Fig. 3.4F) aligned in the HP foliation in the freshest, least retrogressed eclogite samples 152LS1 is in good agreement with Taconic dates of metamorphic zircon rims reported in the present study (~479 Ma; Fig. 3.4C) and by de Wit and Armstrong (2014) (~483 Ma) (Fig. 3.8). Castonguay et al. (2014) obtained a U–Pb zircon date of ~465 Ma,

which was interpreted to be the age of retrogression of eclogite to amphibolite facies conditions. Although rutile dates are commonly regarded as recording cooling events, it has been demonstrated experimentally that the closure temperature for Pb diffusion in rutile is 640–600°C even when grains were subject to slow cooling rates (Cherniak, 2000; Vry and Baker, 2006). Furthermore, phase equilibrium modeling of the EPMS eclogites indicates that the temperature associated with the peak pressure, and the first stages of decompression, was in the range of ~575°C (Massonne, 2024) which is consistent with temperature estimates of 525–575°C in this study and lower than the rutile closure temperature for Pb. We consider the ~483 Ma date to represent rutile crystallization during eclogite-facies metamorphism, prior to retrograde amphibolite-facies re-equilibration. This interpretation assumes that, had rutile recorded cooling during exhumation, it would have likely displayed younger ages closer to those of titanite and apatite that record exhumation described below.

Rutile in a re-equilibrated eclogite 93LS1 matrix yielded a date of ~500 Ma. This is older than the dates typically associated with subduction-related metamorphism in the Baie Verte Margin of ~465 Ma (Castonguay et al. 2014), and ~480 Ma (de Wit and Armstrong, 2014). The kernel density estimation (KDE) identified multiple age groups ranging from ~770 Ma to ~410 Ma (Fig. 3.4G). This supports the hypothesis that rutile in sample 93LS1 probably recorded thermal events as old as 770 Ma. Age groups highlighted by KDE at ~620 Ma, ~570 Ma and ~510 Ma are compatible with rifting and the onset of hyperextension of the Iapetus margin of Laurentia that culminated in the formation of the Taconic seaway (e.g., Kamo et al., 1989; Castonguay et al., 2010; Van Staal et al., 2013) (Fig. 3.8). These dates are also consistent with zircon dates derived from the EPMS metasedimentary rocks (see previous section) further suggesting the presence of multiple thermal events recorded by the Baie Verte margin prior to subduction.

Rutile from sample 230LS1 could not be dated due to its low U concentrations.

Titanite and Apatite Geochronology—Records of Exhumation

Titanite from eclogite 93LS1 (the same containing the ~499 Ma rutile date) yielded a date of ~459 Ma (Fig. 3.4I), which overlaps with the date of eclogite retrogression to amphibolite facies metamorphism suggested by Castonguay et al. (2014). The concentrations of HREE in titanite, however, are relatively depleted (Fig. 3.6B), which suggests that the titanite crystallized coevally with garnet (Hermann and Rubatto, 2003). In addition, the absence of a negative Eu anomaly in the chondrite-normalized REE profile of titanite is consistent with the absence of plagioclase (Fig. 3.6B). The presence of garnet and absence of plagioclase is characteristic of eclogite facies assemblages in metabasites, and titanite from sample 93LS1 have REE compositions that suggest equilibration with an eclogite-facies assemblage. The relative timing of titanite growth with eclogite-facies minerals is indicated by inclusions of rutile—an eclogite-facies mineral—in titanite in sample 93LS1. Considering that we analyzed titanite separates, we do not know the specific petrographic spatial context of each analyzed titanite; however, all fall along a linear array between common Pb and the lower intercept age of ~460 Ma (Fig. 3.4I) suggesting a single age population. This date could reflect a cooling age due to diffusion of Pb (Warren et al. 2012), or possibly a crystallization age (Kirkland et al. 2020). Many studies have shown that diffusion of Zr and Pb is slow in crystalline, non metamict, titanite, and its closure temperature may be as high as 800°C (e.g., Kohn and Corrie, 2011; Stearns et al., 2015, Hartnady et al., 2019). The mean value of the estimated crystallization temperature is 680°C (Fig. 3.7), which falls below the closure temperature for titanite. Hence, we consider ~459 Ma to be the crystallization age of titanite (after rutile) during decompression related to the exhumation of the Baie Verte Peninsula eclogites.

The Eu anomaly and the HREE negative slope in apatite (Fig. 3.6D) suggest that it formed as part of the retrograde assemblage replacing eclogite mineral assemblage in the presence of plagioclase and absence of garnet. Apatite yielded U–Pb dates of ~452 Ma, which are interpreted as the cooling age below the apatite closure temperature of 550–350 °C (Cherniak, 2010; Chew and Spikings 2015).

Igneous Zircon—Records of Late Taconic Magmatism

The main zircon population of the pegmatite dated at ~ 443 Ma represents a Late Taconic age also reported by Willner et al. (2022). These zircon grains have low Th/U ratios <0.03, which are generally interpreted to indicate a metamorphic origin (Hoskin and Black, 2000; Kelly and Harley, 2005; Rubatto 2017; Yakymchuk et al., 2018); however, it has been shown that Th/U ratios of igneous zircon can be this low, especially in evolved pegmatites (Corfu, 2013). Core and rim domains of zircon grains from sample 205LS1 yield weighted mean ages calculated according to Ludwig (2003) of ~451 Ma and 446 Ma, respectively. Although these weighted mean ages are within uncertainty of each other, the cores and rims could be the result of different growth mechanisms during pegmatite crystallization. The cores have higher LREE contents than typical magmatic zircon; this could reflect interaction with late LREE-enriched hydrothermal and/or magmatic fluids. The zircon La and Sm concentrations (Fig. 3.5) are consistent with those determined to be hydrothermal from other localities that have experienced metasomatic alteration by hydrothermal fluids (Piilonen et al., 2012; Yuan et al., 2018).

3.10.4 Summary of the Taconic P–T–t Evolution

Rutile and metamorphic zircon growth at ~483, and ~479 Ma constrain the age of peak—or close to peak—metamorphism at eclogite facies condition related to partial continental subduction of the EPMS (A-subduction) and development of the early-S2 at ~1.8 GPa and 560–670°C. Titanite

crystallizes at ~459 Ma in equilibrium with a garnet-bearing and plagioclase-free assemblage. Titanite crystallization temperature of 650–775°C has been calculated assuming its growth during decompression starting at ~1 GPa, which is generally considered to be the upper-pressure limit of titanite stability (e.g., Kohn, 2017). Titanite growth marks the early stages of retrograde metamorphism of eclogite to amphibolite facies conditions, in agreement with zircon dates of ~465 for this stage (Castonguay et al., 2014). Apatite growth in a plagioclase-bearing assemblage at ~452 Ma indicates further decompression and retrograde metamorphism during protracted exhumation of the EPMS to shallower crustal levels. Evidence of intrusion of pegmatitic dikes crosscutting the eclogite pods and their metasedimentary host rocks at ~ 443 Ma supports the interpretation that the EPMS underwent substantial magmatism and metasomatic activity caused by hydrothermal fluids recording a Late-Taconic thermal perturbation, possibly related to partial melting.

3.10.5 Late Taconic Magmatism and Implications for Exhumation of the EPMS

In collisional orogens, lower crustal melting can play a crucial role in the exhumation dynamics of subducted continental units (Warren et al., 2008). The thermal perturbation associated with the exhumation of eclogite, particularly the high-temperature (HT) overprint of high-pressure (HP) rocks, has been produced by numerical modeling (e.g., Sizova et al., 2012; 2019) and is consistent with the geologic record of various ultrahigh-pressure (UHP) terrains, where partial melting has promoted the exhumation of deeply subducted continental crust (e.g., Kurz et al., 1998; Wilke et al., 2010; Whitney et al., 2011; Faryad and Fišera, 2015). Partial melting can occur as the subducted slab interacts with the overlying hot asthenosphere and associated fluids, reducing the density and viscosity of the continental crust that rapidly rises to lower crustal levels via a hot inter-plate exhumation channel (Faccenda et al., 2008; Gerya et al., 2008). This interaction can

enhance the buoyancy of the broken-off slab, facilitating its rise. The exhumation mechanisms in these settings are often complex and usually involve diapiric ascent driven by partial melting and buoyancy forces (Sizova et al., 2019). Titanite growing after rutile (Fig. 3.3C) at 459 Ma (Fig. 3.4I) is consistent with decompression of the EPMS eclogites and contemporaneous with slab-break off related magmatism in the upper plate (van Staal et al., 2007), and in the suture zone (Brem et al. 2007). The presence of late Taconic pegmatites intruding at ~443 Ma and crosscutting eclogite boudins, possibly associated with partial melting, in the EPMS further suggests that the exhumation of the subducted crust may have been promoted by melting and increased buoyancy of the slab. Therefore, the dominant mechanism we propose for the EPMS is rapid vertical crustal extrusion in a hot inter-plate exhumation channel.

3.10.6 Tectonic Evolution of The Baie Verte Margin and The Notre Dame Arc During the Taconic Orogeny

The multi-mineral petrochronology approach used in the current study clarifies the relationships between deformation and magmatism in the upper plate (Notre Dame arc) and the lower plate (Baie Verte margin) during the Taconic Orogeny. In previous studies, D1 encompasses Ordovician burial, subduction, and exhumation of the BV margin. We observed different generations of deformation and metamorphism and determined the mineral ages that reflect various tectonic events that accompanied the Taconic orogenic cycle. In particular, this study constrains the timing of subduction and development of the eclogitic foliation S2 at ~ 483–479 Ma. Later deformation using S2 occurred at ~459 Ma during amphibolite-facies metamorphism associated with eclogite exhumation.

The presence of three age groups related to subduction and exhumation in the EPMS (e.g., 483–479 Ma, 459–452 Ma, and ~443 Ma) supports the relationship between tectono-magmatic

records of the lower plate, and magmatic pulses in the upper plate Notre Dame Arc (489–477 Ma; 464–459 Ma; 445–435 Ma) (van Staal et al., 2007) (Fig. 3.8). In particular, the deep burial of the EPMS to mantle depths is coeval with continental arc magmatism preserved in the Notre Dame Arc (489–477 Ma). Exhumation of the subducted continental crust (e.g., the EPMS) to relatively shallow levels correspond to voluminous tonalite–diorite magmatism in the Notre Dame Arc between 464 and 459 Ma related to slab break-off. Late-Taconic magmatic and hydrothermal activity in the EPMS is chronologically related to the third magmatic pulse in the upper plate. The correlation of new data in the current study, and existing data, provides detailed evidence of dynamic interactions between subduction, exhumation, and magmatism, underscoring the complex tectono-magmatic evolution of the Baie Verte margin and the Notre Dame arc.

3.11 Conclusions

The EPMS preserves a record of a complex metamorphic evolution characterized by high-pressure eclogite facies metamorphism followed by retrograde amphibolite-facies conditions. Rutile and metamorphic zircon U–Pb dates of 483–475 Ma constrain the timing of near-peak eclogite metamorphism, whereas titanite and apatite dates of approximately 459 Ma and 452 Ma, respectively, recorded subsequent stages of exhumation and cooling. The presence of Late Taconic pegmatites and leucosomes crosscutting the metasediments at 443 Ma in the Baie Verte margin, and at ~ 455 Ma in the Humber margin, (Brem et al. 2007) suggests that exhumation of the EPMS was facilitated by partial melting and increased buoyancy, consistent with models of crustal extrusion and eduction in a hot inter-plate exhumation channel (van Agtmaal et al., 2023). The cause of the thermal perturbation and late Taconic granitic magmatism was likely related to slab break-off.

The results from our study establish a chronologic link between tectono-magmatic events in the lower plate (BV margin), syn-tectonic magmatic pulses in the upper plate (Notre Dame arc), and slab break-off during the Taconic Orogeny (van Staal et al. 2007), emphasizing how the final stages of the Taconic collision in Newfoundland have distinct expressions at different crustal levels. Overall, this study provides a comprehensive view of the tectonic evolution of the EPMS and its broader implications for the Taconic Orogeny, underscoring the significance of multidisciplinary studies in unraveling complex geological histories.

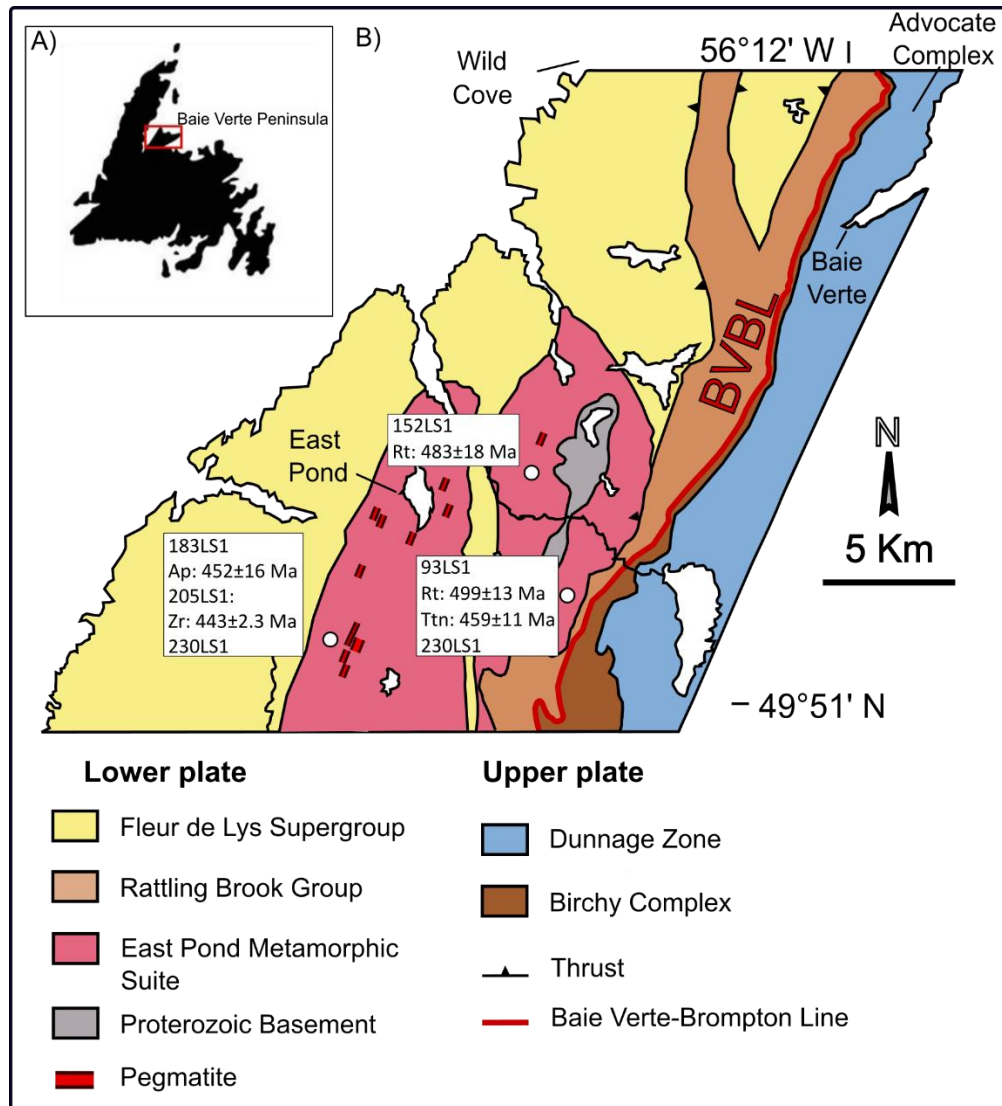


Figure 3.1: A) Location of the Baie Verte Peninsula in Newfoundland. B) Simplified geological map of the Baie Verte Peninsula (modified from Skulski et al., 2010). The open circles show locations of samples 152LS1, 93LS1, 205LS1, 183LS1, and 230LS1. Abbreviations: BVBL = Baie Verte Brompton Line. U-Pb dates are reported with associated 2 sigma errors.

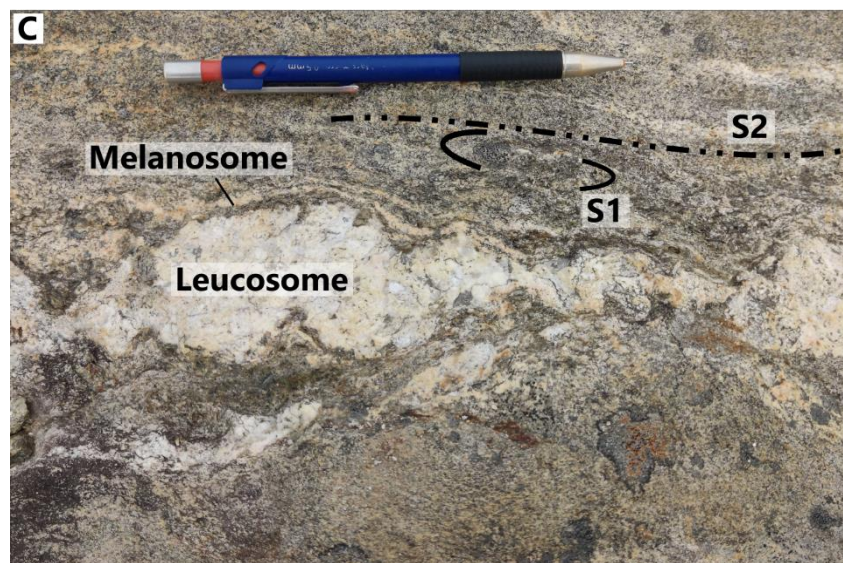
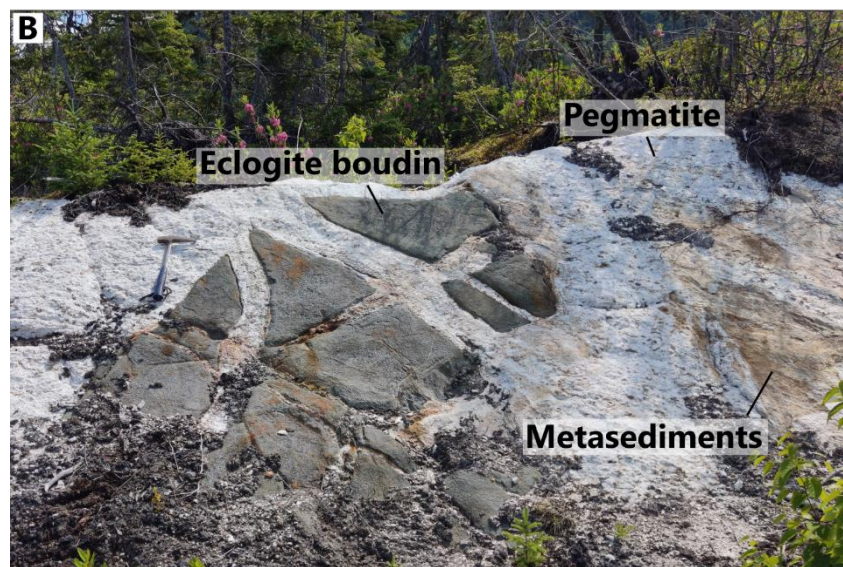
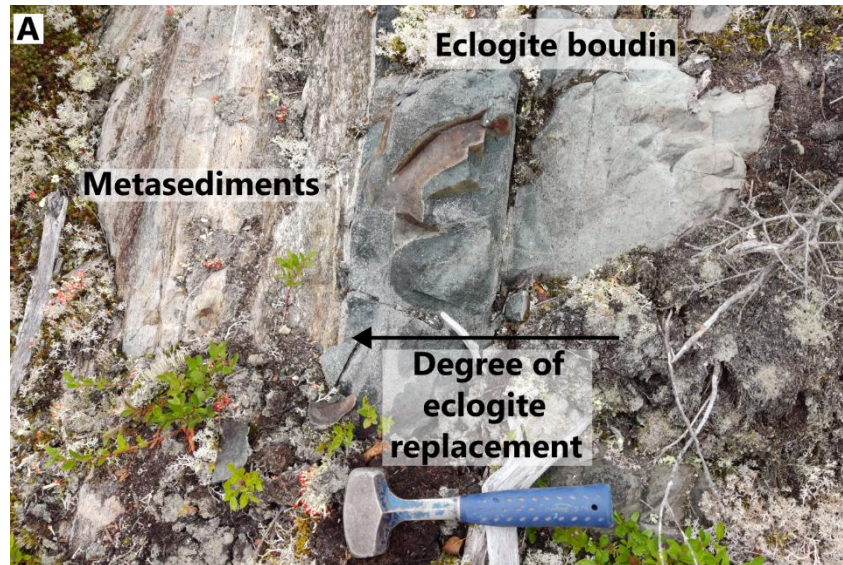


Figure 3.2: (A) Contact between eclogite boudin and metasediments in the East Pond Metamorphic Suite. The arrow indicates the increase in the degree of amphibolite re-equilibration of eclogite, note that towards the contact with the host rock, the fresh eclogite (right side) is gradually replaced by amphibolite (left side). (B) Pegmatite crosscutting the eclogite boudin. Rafts of metasediments are included in the pegmatite. The geological hammer, used as a scale, is on the picture left side. (C) Migmatite consisting of leucosome and melanocratic selvage developed at the contact with the metasediments. The leucosome is elongated and boudinaged in the direction of S2. S1 is locally preserved and is deformed by small-scale, isoclinal F2 folds.

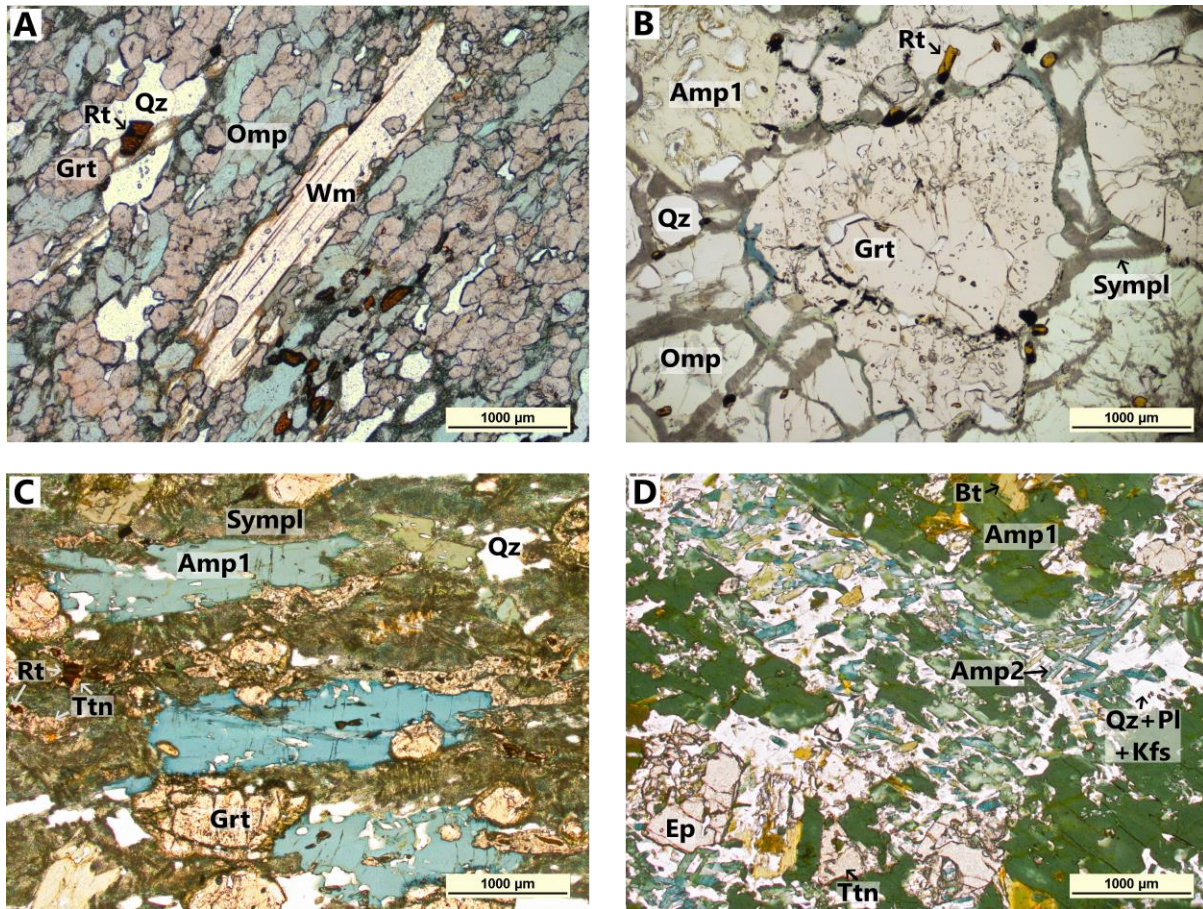


Figure 3.3: Photomicrographs of eclogite samples recording an increasing degree of amphibolite-facies metamorphic overprint from A) D). Pictures are taken in PPL. A) Sample 152LS1: S2 eclogitic foliation marked by Omp+Grt+Phg+Qz+Rt±Ap. B) Sample 230LS1: granoblastic eclogite comprising poikiloblastic garnet including Rt, Qz, and Amp1, omphacite with rutile inclusions, and xenoblastic matrix amphibole. Symplectite develops surrounding omphacite. C) Sample 93LS1c: amphibole1 marks the foliation S2; Amp+Pl±Bt symplectites replace omphacite and phengite; and titanite rims surround rutile. D) Sample 183LS1: coarse amphibole1 crystals are replaced at the grain boundaries by Amp2-Pl-Kfs aggregates.

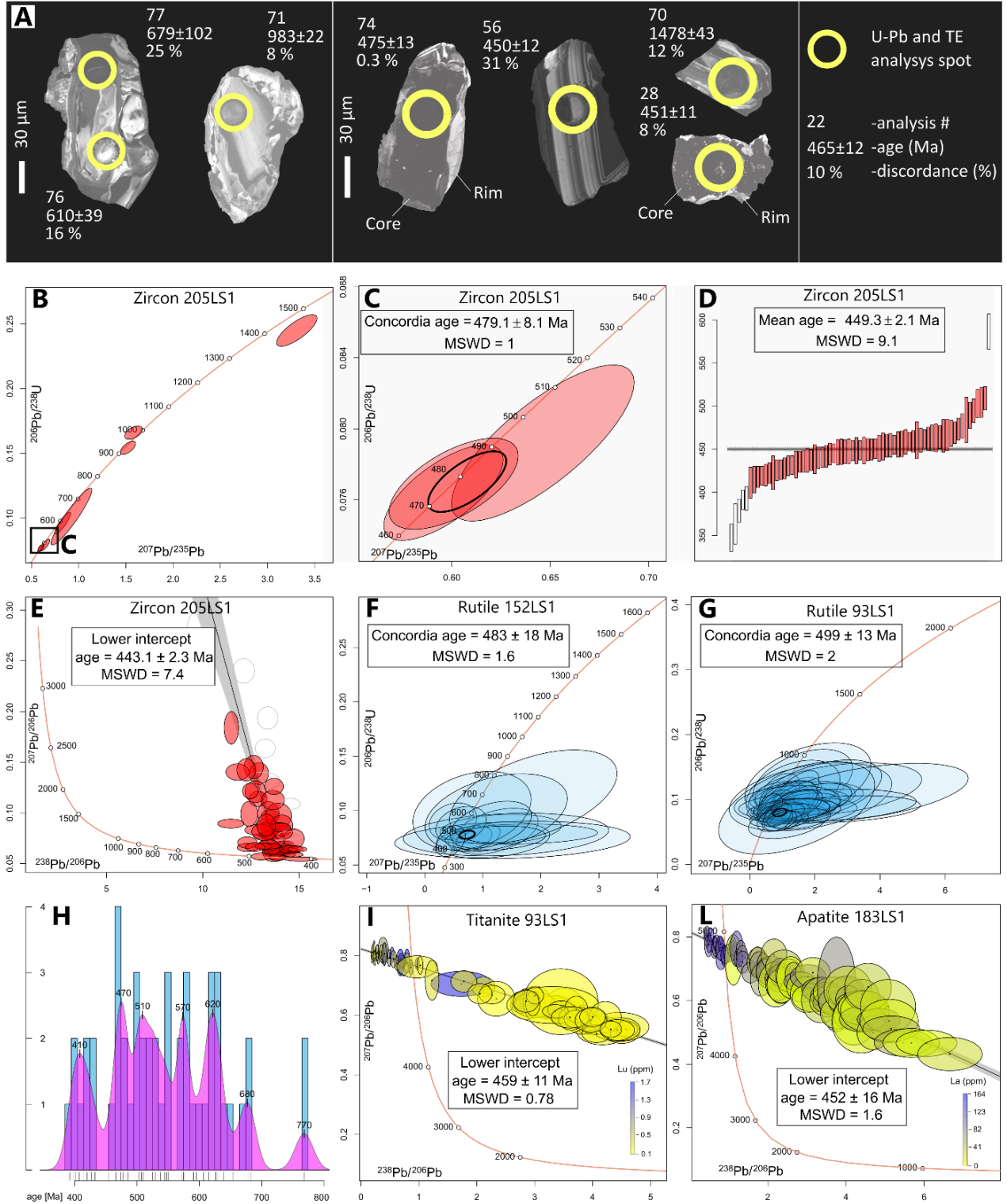


Figure 3.4: (A) Representative CL images of zircon grains from the investigated pegmatite. Yellow circles mark U-Pb and trace elements LA-ICPMS spot analyses. $^{206}\text{Pb}/^{238}\text{U}$ dates (Ma) and the

relative 2σ error, spot number and discordance (%) are reported for each spot. Wetherill concordia diagrams (*B, C, F*), Tera-Wasserburg (T-W) concordia diagrams (*E, I, L*), weighted mean plot (*D*), and kernel density estimation (KDE) diagram for samples 205LS1, 93LS1, 152LS1, and 183LS1 were plotted using IsoplotR (Vermeesch 2018). Titanite and apatite U-Pb data are colored according to their Lu and La concentrations, respectively. Error ellipses are plotted at 2σ . See Table A5 – IV for detailed data of each spot analysis.

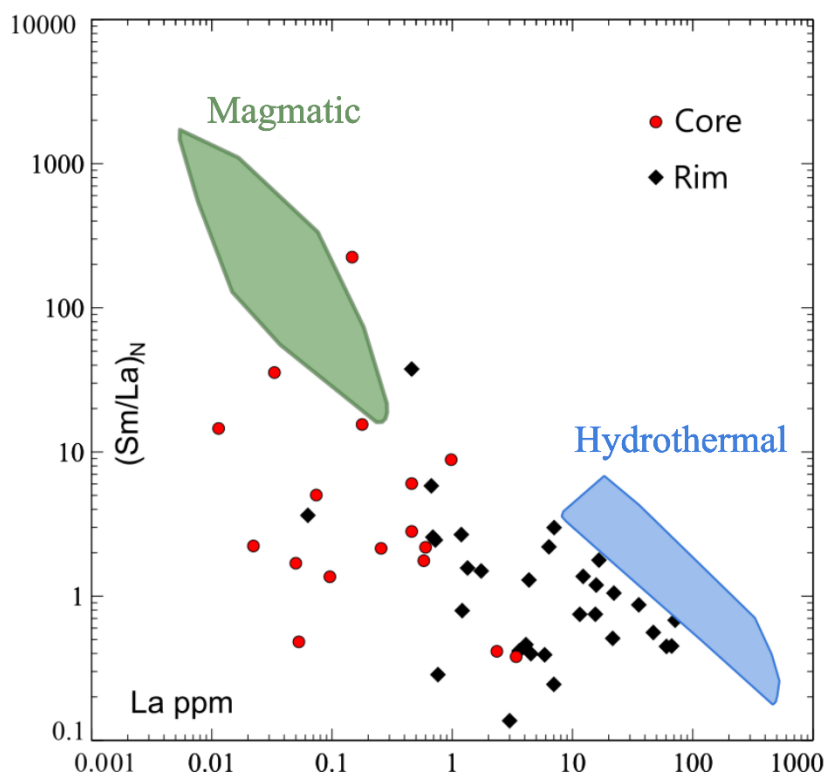


Figure 3.5: $(\text{Sm/La})_N$ vs. La diagram for the main zircon population in pegmatite sample 205LS1. The two outlined areas are defined by Hoskin (2005). Sm and La concentrations are normalized with chondrite values from Anders and Grevesse (1989).

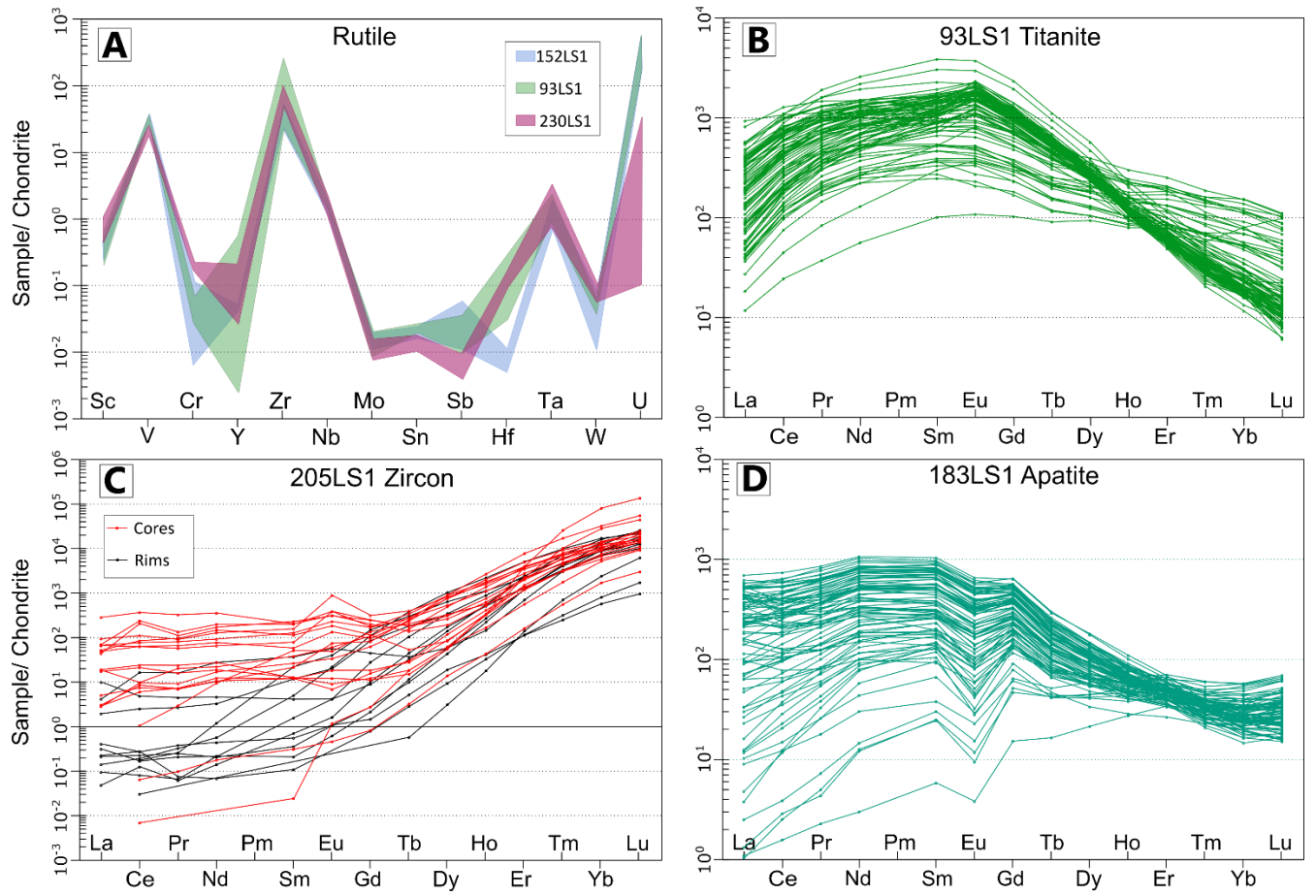


Figure 3.6: A: Chondrite normalized REE profile plots for samples 205LS1, 93LS1, 152LS1, and 183LS1. Chondrite values used for normalization are from Anders and Grevesse (1989).

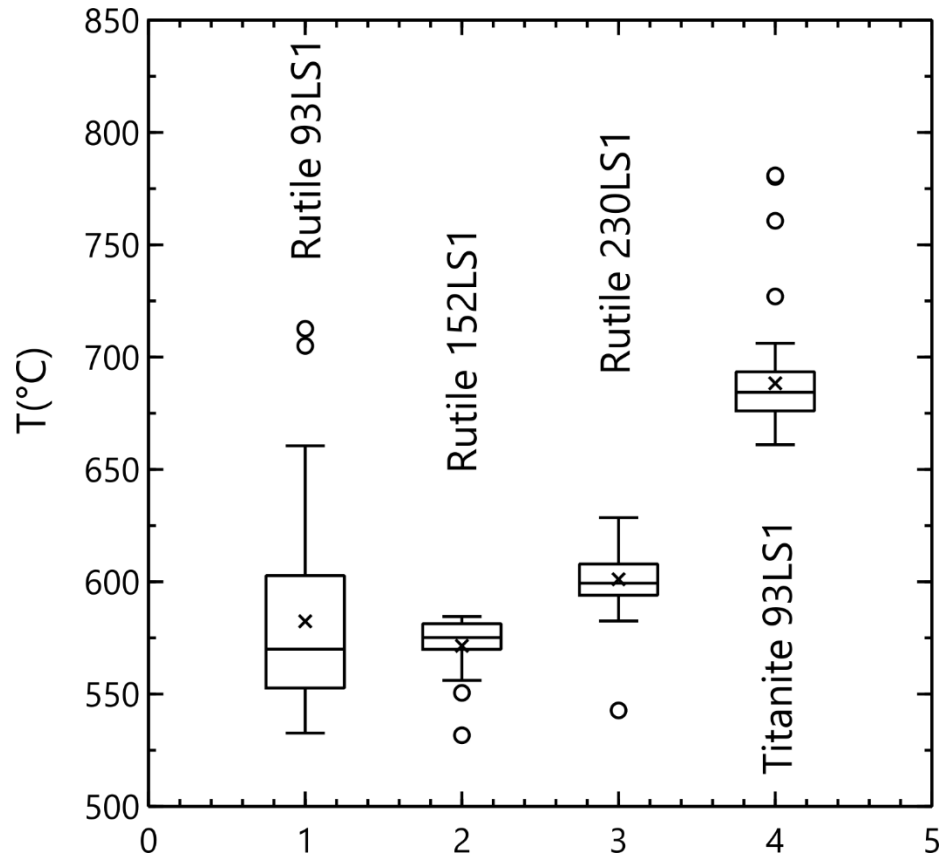


Figure 3.7: The box plot summarizes Zr-in-rutile and Zr-in-titanite thermometry data for samples 93LS1, 152LS1, and 230LS1. Data plotting outside of 1.5 times the IQR are considered outliers. Rutile and titanite temperatures were calculated using the calibrations from Tomkins et al. (2007) and Hayden et al. (2008), respectively.

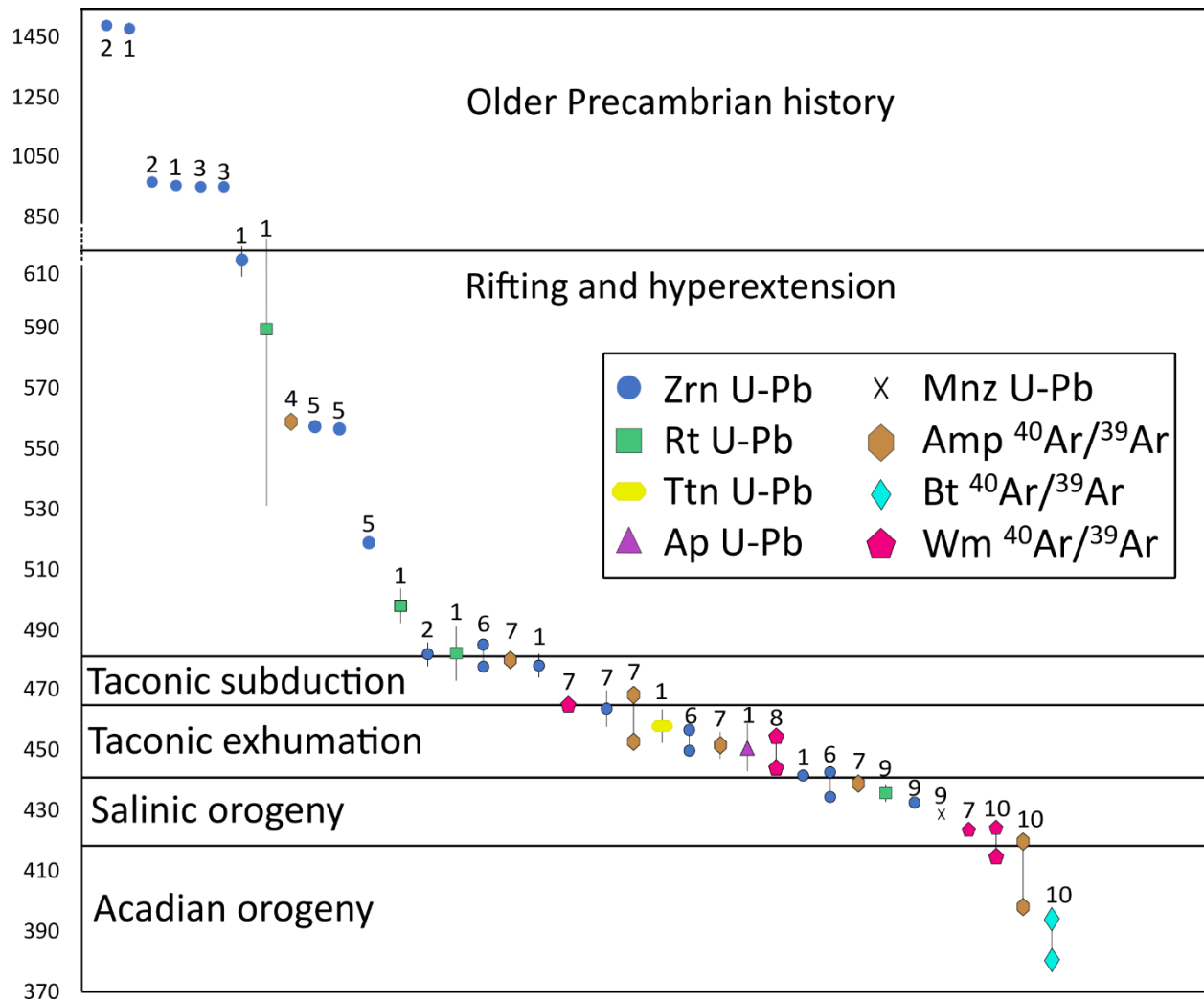


Figure 3.8: Compilation of relevant geochronology data of the Fleur de Lys Supergroup and Dunnage Zone. ¹This study; ²De Wit and Armstrong, 2014; ³Strowbridge et al., 2021; ⁴Castonguay et al., 2010; ⁵van Staal et al., 2013; ⁶van Staal et al., 2007; ⁷Castonguay et al., 2014; ⁸Willner et al., 2022; ⁹Cawood and Dunning, 1994; ¹⁰Dallameyer 1977. Mineral abbreviations from Whitney et al., 2010.

Chapter 4: Tectono-metamorphic evolution of the Baie

Verte Margin, Newfoundland

Summary

A new structural model is presented for the Baie Verte margin in Newfoundland, a segment of the Early Paleozoic Laurentian continental margin that was subducted during the Ordovician Taconic orogeny. The region is divided into three tectono-metamorphic units: the East Pond Metamorphic Suite (EPMS) basement, EPMS cover, and the Fleur de Lys Supergroup (FdLS), each of which experienced distinct metamorphic and structural histories. Early D1, occurring between c. 483 and 475 Ma, is marked by high-pressure metamorphism across all units, with the EPMS cover recording eclogite-facies conditions. Late D1 saw the decoupling of these units, with decompression in the EPMS basement and FdLS, and continued re-equilibration at UHP conditions in the EPMS cover. The D2 phase, spanning c. 475–452 Ma, is associated with retrograde metamorphism in the EPMS cover and Barrovian-style metamorphism in the FdLS, with coupling between the two units occurring along a D2 shear zone. Later deformation phases, D4 and D5, record additional tectono-metamorphic activity related to the Acadian and Neo-Acadian orogenies. This research contributes to the understanding of the prolonged and dynamic tectonic history of the Baie Verte margin, shedding light on the processes driving differential exhumation of tectonic units during subduction, exhumation, and orogenesis at ancient continental margins.

4.1 Introduction

The Ordovician Taconic orogenic belt was developed in the Appalachians along the eastern margin of Laurentia and currently stretches from Alabama to Newfoundland. In the Baie Verte Peninsula, Newfoundland (Fig. 4.1), the Taconic orogeny records the closure of the Taconic seaway and the collision of the Laurentian margin with a magmatic arc over an east-directed subduction zone (Hibbard, 1983; van Staal et al., 2012, 2013). The Taconic orogeny represents the earliest orogenic cycle in this part of the Appalachians and, as such, was subjected to extensive structural and metamorphic overprinting by subsequent orogenic cycles. The complexity of the geochronologic, metamorphic, and structural records has hindered a comprehensive understanding of the tectono-metamorphic evolution of the Baie Verte Peninsula. Although many general features have been identified by previous authors (e.g. Bursnall and de Wit, 1975; de Wit, 1980, Hibbard, 1983), the detailed geometry within and between tectonic units remains unclear, and the relationship between deformation and metamorphic evolution over time is still poorly understood and contentious (Jamieson and Vernon, 1987; Stallard, 1998).

This contribution presents a new model for the tectonic evolution of the Baie Verte margin that integrates new structural data and observations from field mapping. The model describes tectonostratigraphy, regional relationships between, domains recording high-pressure and Barrovian metamorphism, intervening high-strain zones, and the polyphase deformation, which is integrated with existing structural, geochronological, and P-T-t data sets. The main goal of this study is to advance our comprehension of the polyphase tectono-metamorphic evolution of the Baie Verte margin by integrating the structural, petrologic, and geochronological data. In addition, the results contribute to broadening our understanding of how subduction and collision dynamics shape the tectonic architecture of continental margins and provide insights into the global tectonic

processes that drive orogenesis, refine models of P-T-t evolution and their significance for analyzing ancient mountain-building events.

4.2 Geological Setting

The western Baie Verte Peninsula represents the remnants of a segment of the Early Paleozoic passive margin of Laurentia, prior to the closure of the Iapetus Ocean, and is referred to as the Baie Verte Margin (Fig. 4.1). This segment of the Laurentian margin was subjected to a different tectonic evolution than the other margin segments preserved in Newfoundland, which are referred to as the Humber margin (van Staal and Zagorevski, 2020). The Baie Verte margin consists of Proterozoic Laurentian basement rocks (East Pond Metamorphic Suite), unconformably overlain by rift-to drift related cover sequences (Fleur de Lys Supergroup), which were variably metamorphosed and deformed as part of the lower plate during the Ordovician Taconic orogeny (van Staal et al., 1998; 2009; Zagorevski and van Staal, 2011) (Fig. 4.1). The tectonic boundary between the Baie Verte margin and the collided upper plate rocks of the Baie Verte oceanic tract (BVOT) and associated magmatic arc (Notre Dame arc) is marked by the Baie Verte-Brompton Line, a long-lived tectonic lineament interpreted as the Taconic suture zone (Williams and St. Julien, 1982; Willner et al., 2022) (Fig. 4.1).

The East Pond Metamorphic Suite comprises Mesoproterozoic granitoids and migmatites, overprinted by late Mesoproterozoic Grenvillian metamorphism, a sequence of Tonian metasediments and volcanoclastic rocks and younger mafic dikes generally inferred to be related to the opening of the Iapetus Ocean (de Wit, 1980; de Wit and Armstrong, 2014; Strowbridge et al., 2022). Preservation of Early to Middle Ordovician eclogitized mafic bodies demonstrates deep

subduction of the East Pond Metamorphic Suite during the Taconic orogenic cycle (Castonguay et al., 2014; de Wit, 1980; de Wit and Armstrong, 2014; Chapters 2 and 3).

The Fleur de Lys Supergroup, which structurally overlies a metaconglomerate (de Wit, 1974, 1980; Hibbard, 1983), comprises the Birchy Complex, which is interpreted as part of an ocean-continent transition unit, the Rattling Brook Group (an extensional allochthon), Old House Cove, and White Bay groups, which represent para-autochthonous continental margin units (Skulski et al., 2015; van Staal et al., 2013) (Fig. 4.1). The metamorphic history of the Fleur de Lys Supergroup involves several stages that record amphibolite and greenschist facies conditions. However, the relationships between the structural and metamorphic evolution of the Fleur de Lys Supergroup have remained unclear, which has led to contrasting interpretations (e.g., de Wit 1976a, 1976b; Jamieson and Vernon, 1987; Stallard, 1998).

4.2.1 Overview of The Existing Tectono-Metamorphic Framework of The Baie Verte

Peninsula

The structural evolution of the Baie Verte peninsula is complex and characterised by a polyphase deformation history. Up to seven deformation phases have been recognized by some workers, which are generally consolidated into four main deformation events in most studies (e.g., Bursnall and de Wit, 1975; Hibbard, 1983; Castonguay et al., 2014; Skulski et al., 2015; Piasecki, 1988; Willner et al., 2022).

The earliest deformation phase (D1) is generally associated with the formation of eclogite and hence, attributed to deep subduction and underthrusting of part of the Laurentian continental margin. Early structures in the Birchy Complex and Rattling Brook Group developed under high-pressure greenschist to amphibolite facies conditions, whereas eclogite facies rocks occur in the

East Pond Metamorphic Suite (Hibbard, 1993; Jamieson, 1990; Willner et al., 2022), which are the focus of this study. Thermobarometric estimates based on a regional study of the eclogites suggest that this event occurred at c. 2.8 GPa, and 620 °C (Chapter 2), which contrasts with the results: c. 1.9 GPa, and 575°C, recently published by Massonne (2024) based on thermobarometry of biotite-bearing eclogite outcrops. The age of peak eclogite metamorphism is constrained by U-Pb rutile and zircon geochronology between 483–475 Ma (Chapter 3; de Wit and Armstrong, 2014). Late D2 deformation reflects amphibolite to granulite facies retrogression at c. 1.5 GPa, and 860°C, between 459–452 Ma, and is associated with decompression and partial hydration during early exhumation of the East Pond Metamorphic Suite (Chapters 2 and 3). This stage was shortly thereafter followed by the intrusion of late orogenic pegmatites at c. 443 Ma, contemporaneous with a pulse of granitoid magmatism during the third magmatic phase of the Notre Dame magmatic arc (Chapter 3; Whalen et al., 2006; Brem et al., 2007; van Staal et al., 2007).

The D3 structures (D2 of Skulski et al., 2015) are represented by regional-scale upright tight to isoclinal folds, accompanied by amphibolite facies conditions in the East Pond Metamorphic Suite and enveloping rocks. The D3 phase also includes bivergent fault zones with movements directed toward both the southeast and northwest, inferred to have formed between 439 and 425 Ma (Dallmeyer, 1977; Cawood and Dunning, 1993; Castonguay et al., 2010, 2014; Skulski et al., 2015; 2017, Willner et al, 2022).

The D4 deformation (DL of Hibbard, 1993; D3 of Skulski et al., 2015 and Castonguay et al., 2014) is represented by asymmetric, upright chevron F4 folds associated with sinistral oblique reverse (east directed) shear zones (Kidd, 1974; Bursnall and de Wit, 1975; Kidd et al., 1978; Hibbard, 1983; Anderson, 1998). The fifth deformation phase (DL of Hibbard, 1983; D2 and D3

of Anderson et al., 2001) is thought to have been initiated during Devonian extension under a dextral oblique regime, accompanied by amphibolite-facies metamorphism (Skulski et al., 2015b; Anderson et al., 2001; Waldron et al., 1998; Goodwin and Williams, 1996).

There is an ongoing debate in the literature concerning the timing of garnet and albite porphyroblast growth in the Fleur de Lys Supergroup, with various studies offering divergent interpretations (Bursnall and de Wit, 1975; Hibbard, 1983; Jamieson and Vernon, 1987; Stallard, 1998). Albite growth has often been described as continuous throughout the deformation history, while garnet growth is considered more episodic. Jamieson and Vernon (1987) proposed a brief, synchronous growth stage for both garnet and albite during S3 formation, whereas Stallard (1998) linked albite growth to the final deformation stage.

In this contribution, we reconstruct the tectono-metamorphic evolution of the Baie Verte margin, focusing on the eclogites and their enveloping rocks. By integrating structural, petrologic, and geochronological data, we provide a comprehensive model for the region's complex orogenic history, providing new insights into the interplay between high-pressure metamorphism, deformation phases, and the broader tectonic framework.

4.3 Methods

This study presents new structural observations that cover approximately 750 km² between the towns of Fleur de Lys, Westport, and the Baie Verte-Brompton Line (BVBL) in the Western Baie Verte Peninsula (Fig. 4.1). Lithological and structural observations, including structural measurements, were collected from road cuts, hills, coastline outcrops, and several traverses across the study area. Relationships between microstructure and metamorphic mineral

assemblages were determined by petrographic microscopy (e.g., Passchier and Trouw, 2005; Vernon, 2018).

4.4 Results

Figure 4.1 illustrates the structural array of the Baie Verte margin. The tectonic model is based on the structural and petrologic observations outlined in the following three sections. The first section addresses the tectono-metamorphic units, including their characteristic lithologies, present configuration, and tectonic boundaries. The second section describes regional-scale structural patterns. The third focuses on the metamorphic evolution, identifying key tectono-metamorphic stages.

4.4.1 Tectono-metamorphic Units of the Baie Verte Margin

Tectono-metamorphic units are defined as groups of metamorphic rocks that display a coherent structural and metamorphic evolution (Spalla et al., 2000; 2005). Three distinct tectono-metamorphic units were identified, based on differences in lithology, metamorphic, and structural histories. These three units are separated by regional-scale shear zones. The tripartite division contrasts with previous studies that grouped the gneissic and granitic basement rocks together with the metasedimentary sequences into a single unit (East Pond Metamorphic Suite). We identified a structurally lower unit composed of gneissic basement rocks, overlain by two allochthonous cover units of predominantly supracrustal rocks (Fig. 4.1).

East Pond Metamorphic Suite Basement

The East Pond Metamorphic Suite (EPMS) of Hibbard (1983) basement consists of distinctive lithologies, including ca. 1450 Ma granitic gneiss (de Wit and Armstrong, 2014), amphibolite

layers and lenses, banded orthogneiss (interpreted as migmatite by Hibbard, 1993; de Wit, 1974; 1980), paragneiss, quartzite, epidote-biotite-quartz boudins, amphibolite, tourmaline-bearing biotite schists, porphyroblastic orthogneiss, and granitoid pegmatites. Detailed mapping revealed that the basement's extent is far greater than previously recognized and exposed in wide windows located in the cores of regional-scale upright F3 folds (Fig. 4.1). The basement displays complex early structures, including intrafolial rootless folds, and records each regional event observed in the overlying cover rocks. The mafic lenses and layers within the basement do not preserve eclogite assemblages in contrast to the immediate cover unit. The tectonic contact between the basement and the overlying cover unit is marked by a zone of ultramylonite that can reach widths of up to tens of meters (Fig. 4.4D).

East Pond Metamorphic Suite Cover

The immediate structural cover unit to the EPMS basement unit includes psammitic and semipelitic schist, Tonian felsic and mafic tuffs (i.e. Strowbridge et al., 2022), banded gneiss, metaconglomerate, semipelitic schist, amphibolite, eclogite, biotite-garnet quartzite, and pegmatite. The monotonous succession of psammitic and semipelitic schists constitutes the bulk of the cover sequence. Preservation of primary sedimentary structures, such as flame structures, rafts, and Bouma sequences, suggests that the layering represents, at least in part, bedding and provides younging indicators (Fig. 4.1A). The metaconglomerate is exposed in the westernmost antiformal core and forms the structural base of this allochthonous cover unit. The metaconglomerate hosts variably retrograded eclogite bodies and grades into the quartzofeldspathic psammite that forms the main component of this structural cover unit.

The banded gneiss, traditionally considered part of the basement (de Wit, 1976; 1980; Hibbard, 1983; 1988), is herein included with the cover sequence due to its gradational transition with the psammites. These gneisses occur near the contact with the basement unit preserved in the westernmost antiformal core, suggesting they represent part of the lower section of the cover. Albite porphyroblasts, characteristic of- and widespread in the Fleur de Lys Supergroup of the upper cover unit (Jamieson, 1987; 1990), occur within the EPMS only in shear zones, tectonic boundaries, and at the margins of amphibolitized eclogites.

Fleur de Lys Supergroup metasediments

The structurally upper cover unit is represented by the Fleur de Lys Supergroup which comprises pebbly psammite, quartzite and schistose psammite, semipelite and pelite, all interlayered with amphibolite. The monotonous schistose psammite and semipelite sequence is the dominant lithology in the Fleur de Lys Supergroup (Fig. 4.3B). The metasedimentary rocks are locally rich in tourmaline and contain staurolite and kyanite porphyroblasts (Figs. 4.3F,G). While cordierite and sillimanite have been reported in the eastern part of the study area (Bursnall, 1975; Kennedy, 1975), they were not observed in this study. Biotite-rich quartzo-feldspathic and layers dominated by biotite and muscovite, interpreted as bedding (Hibbard, 1983), locally preserve primary structures. Albitization is extensive across all lithotypes, with albite porphyroblasts commonly enclosing garnet and preserving relict foliations (Figs. 4.3E, F, H). The tectonic boundary between the Fleur de Lys Supergroup and the East Pond Metamorphic Suite cover unit, referred to as the "Tectonic Schist" by de Wit (1976, 1980), consists of albite-rich two-mica porphyroblastic schists.

4.4.2 Regional Structure of the Baie Verte Margin

Five generations of structures have been identified on the basis of overprinting relationships in the field (Fig. 4.5).

The earliest structure observed in both the East Pond Metamorphic Suite (EPMS) and the Fleur de Lys Supergroup (FdLS) cover sequences is a planar structure (SL), commonly a compositional layering defined by layers rich in mica, quartz and feldspar, this compositional layering is interpreted as bedding (Fig. 4.2A, 4.3A). Younging indicators indicate the presence of both downward- and upward-facing limbs of pre-D3 folds. Other evidence for the existence of two distinct pre-D3 generations of structures is provided below.

D1 is distinguishable only in areas where the dominant S3 foliation is weakly developed, such as in the hinges of regional-scale F3 and F2 folds in the EPMS and FdLS, or in the eclogite boudins in the EPMS. F1 and F2 folds are isoclinal to close structures (Figs. 4.2B, F, 4.3C, 4.4B). Figure 3.4C shows FdLS metasediments preserving the three earliest generations of structures, F1 isoclinal recumbent folds are deformed by F2 folds. F2 folds albite porphyroblast-rich layers, thus, albite porphyroblast growth is inferred to be related to D1 or early during D2.

Along the EPMS-FdLS tectonic boundary, albite porphyroblasts preserve an internal foliation S1 at an angle to the external foliation S2 which envelops them. Sigmoidal albite porphyroblasts and tourmaline needles lying in S2 surfaces are boudinaged along a steeply plunging stretching lineation to the north-east; this suggests oblique shear during D2 with a dextral horizontal component (Fig. 4.4A).

F1 and F2 folds are observed directly in some outcrops (Figs. 4.2F, 4.3B, C, 4.4 B), while in others their existence is indicated by the presence of two distinct post-SL and pre-D3 foliations (Fig. 4.2B).

D3 generally led to the formation of regional-scale tight F3 folds. Pre-D3 structures are thus reoriented and locally transposed into near parallelism with S3, and if so, commonly forming a composite foliation comprising layering, S1, and S2. Gradual regional variations in D3 and pre-D3 structure orientations led to the distinction of northern, central, and southern structural domains (Fig. 4.5). In the northern domain, F3 axial planes dip moderately to steeply to the southeast (Fig. 4.5), while they are sub-vertical in the central domain and dip slightly northwest in the southern domain. The F3 hinge lines plunge shallowly to the northeast in the northern domain, progressively rotating to north-northeast trends with steeper plunges in the central and southern domains (Fig. 4.5).

D4 deformation is heterogeneous and is mainly expressed as centimeter-scale chevron F4 folds which are well developed on the limbs of F3 folds. Even in areas where D4 is more intense, it rarely forms an axial planar cleavage. D5 is associated with open folds and a weakly developed cleavage that dips shallowly to the northeast (Fig. 4.5).

D5 is linked to WNW-ESE trending dextral reverse or normal shear zones.

The kilometer-scale shear zone between the EPMS and FdLS cover sequences, which defines the contact between EPMS and FdLS cover units (Fig. 4.1), is folded by F3. Its kinematic reconstruction is complicated by the presence of multiple superposed generations of planar and linear features and conflicting shear-sense indicators. Similarly, numerous shear zones (sub)parallel to S3 occur throughout the rocks of the Baie Verte margin, and contain conflicting shear-sense indicators, suggesting multiple stages of re-activation with the most recent reactivation generally dextral. Shear zones at the boundary between the EPMS and the Rattling Brook Group (Fig. 4.1, 4.4C) show top-to-the-east dextral shear sense indicators.

4.4.3 Generations of Structures and their Relationships to Growth of Metamorphic Minerals

The various generations of structures are associated with superposed metamorphic events, which are critical for unraveling the tectono-metamorphic evolution of the region and provide a framework for developing a comprehensive tectonic model.

East Pond Metamorphic Suite Basement

In the EPMS basement gneisses, D1 relicts are represented by pre-kinematic garnet (including rutile), rutile, and tschermakite porphyroblasts, which are enveloped and locally re-aligned into parallelism with S2, and by resorbed rutile cores included within S2-parallel titanite grains in the mafic boudins.

The S2 foliation in the felsic EPMS basement gneisses is delineated by quartz and clinozoisite-rich metamorphic layers that envelop pre-kinematic garnet, rutile, and amphibole porphyroblasts. Amphibole porphyroblasts characterized by a tschermakite core and a hornblende rim, with an internal foliation marked by rutile and clinozoisite that is oblique to the external S2, are locally preserved.

East Pond Metamorphic Suite Cover

In the eclogites boudins, S1 is defined by discontinuous layers rich in eclogite-facies minerals such as garnet, omphacite, and quartz (Chapter 2) (Fig. 4.2B). In some of the studied eclogite samples, garnet porphyroblasts contain clinozoisite and titanite inclusions. In the metasediments, S1 is delineated by the preferred dimensional orientation of rutile- and phengite-rich films transposed by S2. Garnet porphyroblasts are enveloped by a foliation S2 rich in rutile and phengite (Fig. 4.2H). Xenoblastic epidote porphyroblasts pre-kinematic with respects to S2 may also be associated with this metamorphic assemblage.

In the eclogites, F2 folds deform the S1 and S2 foliations characterized by eclogitic minerals. The axial plane foliation (S2) to F2 folds is defined by the garnet-omphacite-quartz-rutile-phengite assemblage (Figs. 4.2B, C). In some eclogite pods, cores with fresh eclogite mineral assemblages and katophorite-rich mantles are preserved. In these rocks, S2 is defined by a bluish katophorite-bearing foliation that is parallel to the eclogitic S2 present in the boudin cores (Fig. 4.2D). In the metasediments, S2 is characterized by the preferred orientation of white mica, biotite, and quartz (Figs. 4.2G, H).

Late Taconic pegmatite intrusions crosscut the mafic boudins and are spatially associated with leucosome in the host metasedimentary rocks, which suggests a genetic link to partial melting and high-temperature metamorphism (Chapter 3). These intrusions have been observed in the southern part of the westernmost antiformal core, where both EPMS cover, and basement are exposed. Evidence of partial melting, such as leucosome surrounded by a biotite-rich melanocratic rim, is here locally preserved in gneisses of the EPMS basement.

F3 folds deform S2 (Fig. 4.2E) in the eclogites, with S3 defined by a preferred dimensional orientation of hornblende, plagioclase, epidote, biotite, white mica and titanite. Hornblende-rich veins, locally crosscut the eclogite fabric (Fig. 4.2B).

Fleur de Lys Supergroup metasediments

In the metasedimentary rocks, F1 isoclinal, recumbent folds are best preserved in the hinges of large F3 folds and are mainly highlighted by folded albite-rich layers (Figs. 4.3B, C). In these rocks, S1 is defined by rutile, phengite, and quartz (Fig. 4.3D, E, F, G).

Albite porphyroblasts are enveloped by the S2 foliation and have a preferred dimensional orientation parallel to their internal foliation S1. The internal foliation is discontinuous and at an

angle to the S2 external transposition foliation marked by white mica and biotite (Fig. 4.3E). Garnet porphyroblasts occur as inclusions in albite, they include trails of S1 foliation which is continuous and parallel with the external S1 foliation (Fig. 4.3E). In the matrix, S1 is a relict foliation marked by white mica, which is crenulated by S2 and preserved in the S2 lithons (Fig. 4.3D). Similarly, albite porphyroblasts in mafic pods are enveloped by S2 and have an internal S1 foliation marked by oriented rutile, amphibole, epidote, and post-kinematic garnets which have grown over the S1 foliation (Fig. 4.3H). The amphibole-rich S2 and matrix wraps around albite porphyroblasts, as well as barrosite and tschermakite porphyroblasts. Garnet has inclusions of clinozoisite and titanite and more commonly rutile and quartz. Overall, S1 is mainly preserved as a relict foliation within garnet or albite porphyroblasts and is marked by rutile-quartz-white mica $\pm$ epidote or as a transposed foliation in the metasediments.

In the metasediments, the S1 differentiated metamorphic layering rich in albite porphyroblasts, inferred to have formed late during D1, are folded by F2 (Fig. 4.3C). S2 is defined by aligned white mica and biotite (Figs. 4.3D, E, G). A sample from the northern FdLS preserved subidioblastic staurolite with sigmoidal S2 inclusion trails marked by quartz, white mica and opaque minerals, continuous with the external foliation. (Fig. 4.3G). Whereas a sample containing kyanite was detected at the tectonic boundary between the EPMS and FdLS along the western limb of the westernmost antiform (Fig. 4.1). In this sample, kyanite is aligned with the S2 foliation; the internal foliation is continuous with the external foliation. Both internal and external foliations are defined by the alignment of white mica, biotite, quartz, and opaque minerals. The S2 foliation and the deformed kyanite grains wrap around albite porphyroblasts.

The S2 foliation is defined by green hornblende in the mafic pods, which wraps around albite porphyroblasts. However, green hornblende also occurs as inclusions in the albite porphyroblasts,

where it forms a discontinuous foliation parallel to S1, sometimes associated with epidote (Fig. 4.3H). Hence, hornblende was present during D1 and D2.

In the metasedimentary rocks, S3 is marked by oriented biotite and white mica (Figs. 4.2G, 4.3F). Pseudomorphic chlorite grew as replacement of garnet and biotite outlining S1 and S2 foliations in the EPMS and FdLS metasediments. Post-kinematic idioblastic chloritoid is oriented at a high angle to S3 in the FdLS.

4.5 Discussion

4.5.1 Tectono-Stratigraphy and Regional Structure

The Laurentian Baie Verte margin comprises a composite tectonostratigraphy defined by at least three internal tectono-metamorphic units, which are separated by shear zones. From the structurally lowest to highest levels, the main units and associated shear zones in the tectono-stratigraphy are as follows: (i) the East Pond Metamorphic Suite basement, interpreted as Mesoproterozoic Grenvillian basement rocks (Hibbard, 1983); (ii) an ultramylonite zone that developed in both the basement and overlying cover units; (iii) the East Pond Metamorphic Suite cover unit, predominantly consisting of metasediments with subordinate mafic boudins and metavolcanic rocks; (iv) a shear zone composed of highly schistose and albitized rocks derived from both the EPMS and the structurally overlying cover rocks of the Fleur de Lys Supergroup; and (v) the Fleur de Lys metasedimentary cover rocks, which include elongated, layer-parallel mafic boudins.

The regional structure of the Baie Verte margin is dominated by a macroscopic northeast-trending upright F3 folds such that the structurally deepest levels are exposed in the cores of two large periclinal antiforms (Figs. 4.1, 4.4) separated by tight intervening synforms cored by the

Fleur de Lys Supergroup. The regional and smaller-scale F3 structures folded and significantly reoriented the shear zones between the three recognised tectono-metamorphic units. Hence, the shear zones formed before D3. The hinge lines of the F3 folds in the investigated area generally plunge to the northeast. Local variations in plunge occur in the different structural domains, which at least in part, is due to subsequent deformation during the F4 and F5 folding events, and formation of late shear zones. Preservation of nearly recumbent F1 and F2 folds in the hinges of F3 antiforms suggests that the enveloping surface of the structural stack comprising the three major tectonic units probably had a relatively shallow dip prior to F3 folding. After unfolding the F3 folds, the composite S1/S2 foliation preserved in the limbs of the F3 folds acquires a sub-horizontal dip and an approximately NE-SW trend for the stretching lineation. These E-W shear direction indicators, together with a dextral horizontal component along the EPMS cover-FdLS boundary (Fig. 4.4A), suggest tectonic emplacement of the EPMS beneath the FLDS along a normal-sense shear zone.

4.5.2 Tectono-Metamorphic Evolution

The tectono-metamorphic evolution described in this study is based on the integration of our new structural (Fig. 4.5), petrologic, and geochronologic data (Chapters 2 and 3) with the existing data. This approach aims to address some of the current knowledge gaps by linking the evolution of the three tectono-metamorphic units through their observed structural and petrologic features.

The presence of early D1 medium- to high-pressure (MP to HP) mineral assemblages, such as garnet, rutile, and phengite, is a common feature across all tectono-metamorphic units. Early D1 metamorphism in the East Pond Metamorphic Suite (EPMS) cover unit occurred under eclogite-facies conditions, as evidenced by garnet with rutile inclusions, omphacite, and phengite

growth in mafic boudins (Figs. 4.2C, D), and by garnet with rutile inclusions and phengite in metapsammities (Fig. 4.2H). Locally preserved clinozoisite and titanite inclusions in garnet from both the EPMS cover and Fleur de Lys Supergroup (FdLS) may represent (pre-?)D1 stages of the prograde metamorphic burial path, which culminated at pressures of c. 2.8 GPa, and 620 °C in the EPMS cover unit (Chapter 2), and between 0.7–0.8 GPa, 450°C (Jamieson, 1991) to 1.8 GPa (Willner et al., 2012, unpublished data) in the FdLS cover unit. Although fresh eclogites are exclusively observed in the EPMS cover unit, the disequilibrium textures in the mafic boudins of the EPMS basement unit—such as resorbed garnet, amphibole, plagioclase symplectites, and titanite rims around rutile—resemble some of the strongly retrograded eclogites of the cover unit (e.g. de Wit, 1980). This suggests that the basement either did not reach eclogite-facies conditions or was subjected to a more extensive re-equilibration under amphibolite-facies conditions. If the latter, this may be due to the late D2-related thermal perturbation, which resulted in the intrusion of voluminous pegmatites and formation of migmatites, which are widespread in the EPMS basement compared to the cover. Rutile and zircon dating constrain the timing of D1 in both the EPMS basement and cover units to between c. 483–475 Ma (Chapter 3; de Wit and Armstrong, 2014). However, the absence of geochronological and pressure-temperature (P-T) data for D1 in the EPMS basement and FdLS precludes definitive correlations between these units.

In the EPMS cover, the S2 foliation is defined by eclogite-facies minerals in the fresh eclogite boudin cores (Fig. 4.2C). Toward the boudin rims, these high-pressure minerals are progressively replaced by lower-pressure phases (Figs. 4.2D, E). The fabric defined by these lower-pressure minerals (e.g., katophorite) remains parallel to the eclogitic S2 foliation, suggesting that D2 was a protracted event linked to the exhumation of the EPMS cover. The β -shaped P–T path reconstructed for the EPMS eclogites during D2 forms a beta-shaped trajectory, beginning at

peak conditions of ~2.8 GPa and 620 °C, followed by near-isothermal exhumation to ~2 GPa and 660°C. This was followed by heating at ~1.5 GPa and 860 °C, and eventually retrogression under amphibolite-facies conditions in the presence of fluids (Chapter 2). The timing of the late D2 stages, associated with the thermal perturbation and re-equilibration of the eclogites to lower pressures and temperatures, is constrained by U-Pb dating of zircon, titanite, and apatite, yielding ages between c. 465 Ma and 452 Ma (Castonguay et al., 2014; Chapter 3).

In the Fleur de Lys Supergroup (FdLS), D2 was accompanied by regional amphibolite-facies metamorphism, following late D1 decompression as indicated by late-D1 albite porphyroblastesis. The S2 foliation is associated with: (i) the growth of hornblende rims around tschermakite cores and marked by aligned hornblende in the foliation that wraps around albite porphyroblasts in the mafic boudins; (ii) the folding of albite-rich layers, interpreted as products of late D1 decompression; (iii) kyanite growth at the tectonic boundary between the EPMS and FdLS, inferred to represent the deepest tectonic levels reached by the FdLS; and (iv) staurolite growth in the northern part of the FdLS. The presence of kyanite at the interface between the EPMS-FdLS cover units and staurolite in the northern part of the peninsula could be explained in two ways: either the lower part of the sequence re-equilibrated at higher pressures than the upper sections, or basal shearing locally induced tectonic over-pressure at the boundary (e.g., Schmalholz and Podladchikov, 2013).

In the EPMS basement unit, D2 is also consistent with pressure decrease and amphibolite-facies metamorphism, as evidenced by a foliation dominated by clinozoisite and quartz wrapping around garnet and hornblende porphyroblasts with tschermakitic cores. The lack of precise geochronological constraints on D2 in both the FdLS and the EPMS basement prevents a definitive correlation between the two units at this stage. However, it can be inferred that while D2 in the

EPMS cover is related to exhumation from peak pressure conditions, in the FdLS—and possibly in the EPMS basement—it reflects a post-decompression stage, because F2 folds late D1 metamorphic layers rich in albite (Fig. 4.3 C), which are interpreted to have grown as a result of breakdown of former Na-rich, higher-pressure phases during decompression (Jamieson, 1991).

D3 is associated with folding and a penetrative amphibolite-facies overprint throughout the Baie Verte margin. In the EPMS cover unit eclogites, S3 is marked by a preferred dimensional orientation of hornblende, plagioclase, epidote, biotite, and titanite, which define amphibolite facies conditions during D3. In addition, hornblende-rich veins locally crosscut the eclogite fabric (Fig. 4.2B), and are also interpreted to be related to the syn-D3 amphibolite facies metamorphism (Chapter 2). Zircon and monazite U–Pb geochronology, along with Ar/Ar mica and amphibole geochronology, constrain this event to between c. 439 and 425 Ma (Dallmeyer, 1977; Cawood and Dunning, 1993; Castonguay et al., 2010, 2014; Skulski et al., 2017; Willner et al., 2022). Hence, D3 deformation occurred during the Silurian Salinic orogenic cycle (e.g. Skulski et al., 2015).

D4 and D5 are not linked to any specific metamorphic events. However, the presence of post-kinematic chlorite and chloritoid growth, along with widespread Devonian ages (e.g., Dallmeyer, 1977; Willner et al., 2022), suggests that the Baie Verte margin was subjected to tectono-metamorphic activity during the Acadian and/or Neo-Acadian orogenies.

4.5.3 Tectonic Model

Peak pressure metamorphism during D1, associated with recumbent isoclinal folding between 483 and 475 Ma, is consistent with subduction of the various units that comprise the Baie Verte margin (Hibbard, 1983; Castonguay et al., 2014; de Wit and Armstrong, 2015; Chapter 3) (Fig. 4.6a).

Folds and foliations defined by garnet, rutile, and, locally, phengite developed during D1 in all identified tectono-metamorphic units (e.g., Figs. 4.3E, F). This indicates that these units were subducted to depths sufficient to form medium- to high-pressure (MP to HP) mineral assemblages. Both the EPMS cover and FdLS locally preserve clinozoisite and titanite inclusions in garnet which may represent early-D1 stages of the prograde metamorphic burial path. The extent of the tectonic coupling during the underthrusting stage is poorly known, however, based on the coherent early-D1 and later D1 stages of the preserved metamorphic record across the three units we propose that the Baie Verte margin underwent initial burial as a coherent continental block (Fig. 4.6a).

Existing estimates suggest that during D1, the Fleur de Lys Supergroup (FdLS) may have reached depths up to c. 40 – 45 km (Jamieson, 1990), while the EPMS cover subducted to depths of c. 90–100 km (Chapter 2). This implies that the tectono-metamorphic units were buried to different depths and that they probably have been shuffled with respect to each other along shear zones, during probably diachronous D1–D2 event(s) prior to their final juxtaposition before the onset of D3 (Fig. 4.6b, c). Based on the substantial difference in the available peak pressure estimates, we suggest that the EPMS cover-FdLS tectonic decoupling occurred during subduction, rather than during exhumation.

Late-D1 albite porphyroblast-rich layers are deformed by D2 (Fig 4.3C), indicating that amphibolite-facies overprinting related to decompression occurred in the FdLS prior to D2. Subsequent Barrovian-style metamorphism developed during D2 in the FdLS, is indicated by the growth of kyanite and staurolite (Figs. 4.3F, G). In the EPMS cover, albite growth occurs during late-D2 after a complex metamorphic D2 metamorphic evolution, initiating under eclogite-facies conditions, progressing through amphibolite/granulite conditions, and concluding under

amphibolite facies conditions between c. 475 Ma and 452 Ma (Chapters 2 and 3). In the EPMS cover, late-D2 is also associated to titanite and plagioclase-amphibole symplectite growth dated between c. 464 and 459 Ma (Castonguay et al., 2014; Chapter 2, 3). In the Baie Verte margin, albite blastesis serves as a structural time marker indicating that late-D1 in the FdLS is coeval to late-D2 in the EPMS cover. These age constraints, together with apatite ages of c. 452 Ma interpreted to be associated to cooling in epidote-amphibolite facies conditions (Chapter 3), indicate that late-D1 in the FdLS and late-D2 in the EPMS cover developed between c. 464 Ma and 452 Ma (Fig. 4.6c).

The contrasting metamorphic record between EPMS cover and FdLS, particularly the absence of eclogites in the FdLS, suggests that the decoupling between the two units occurred prior to the attainment of peak pressure conditions in the EPMS cover, and therefore during subduction (D1), rather than exhumation (D2).

Decoupling and recoupling of tectono-metamorphic units requires movement accommodated by the highly tectonized, mylonitic boundaries between them (e.g., Figs. 4.1, 4.4A, D). We interpret the shear zone at the boundary between the EPMS cover and FdLS as a D2 exhumation-related feature, which has been active during the upwards tectonic escape of a HP sliver (EPMS cover unit), consistent with tectonic emplacement of the preserved EPMS beneath the FdLS. This is inferred in the basis of structural and metamorphic observations, specifically: (i) shear sense indicators along the EPMS-FLDS boundary (Fig. 4.4A) suggest a normal-sense shear zone, where westward displacement of the footwall (EPMS) facilitated its exhumation beneath the FLDS in response to extension during D2; (ii) in the FdLS, S2 overprints albite porphyroblasts,

interpreted to be an exhumation-related feature (Jamieson, 1991), and in the EPMS cover unit, D2 is recorded during exhumation from peak- to lower-pressures typically associated with crustal levels. Hence, the metamorphic evolution during D2 indicates decompression and re-equilibration in amphibolite facies in the EPMS in both units. The existing geochronological constraints on syn-D2 metamorphism in the EPMS cover and structural constraints of the development of the D2 shear zone described above, suggests that EPMS-FdLS cover units were tectonically juxtaposed and recoupled late during D2. Coherent with the development of D2 shear zones in a context of Late Taconic decompression related to exhumation of subducted crustal wedges (Fig. 4.6c).

The β -shaped P–T path of EPMS eclogites indicates a syn-D2 two-stage exhumation where early isothermal decompression transitions into decompression with an increase in temperature (Chapter 2). Heating can be related to mantle upwelling resulting from slab rollback, steepening, or break-off and causes partial melting of subducted rocks (Gerya et al., 2002; Warren, 2008; Sizova et al., 2019). The presence of late Taconic pegmatite intrusions crosscutting eclogite and amphibolite in the EPMS at c. 443 Ma and evidence of partial melting in the metasediments indicate that exhumation of parts of the Baie Verte margin may have been promoted by buoyancy-driven mechanisms related to partial melting of the exhumed continental slices (Chapter 3). Evidence of partial melting is locally preserved in gneisses of the EPMS basement, however, the lack of P-T and geochronology data in the basement metamorphic and magmatic rocks hinders a correlation between this event across the two units.

We interpret that the EPMS cover and FdLS were buried to different depths and exhumed to different extents prior to their juxtaposition before the onset of D3. Disequilibrium textures in the EPMS basement mafic pods strongly resemble those observed in the retrogressed eclogites in the cover, and eclogite occurrence in the basement has been reported by de Wit (1980). This suggests

that the basement may have attained eclogite-facies conditions, but it was subject to later, widespread amphibolite facies overprinting possibly related to voluminous migmatization and pegmatite intrusion. We propose the following two exhumation scenarios to explain the tectonic evolution of the Baie Verte margin during the Taconic subduction and exhumation: (i) Following late D1 detachment, the FdLS was exhumed to crustal levels, while the EPMS basement and cover were subducted to mantle depths. The EPMS basement and cover were subsequently emplaced beneath the by tectonic extrusion along the D2 shear zone, with melt-weakening assisting exhumation (e.g., Möller et al., 2015; Whitney et al., 2015); (ii), detachment of the three tectonic units occurred sequentially, from the top to the bottom of the slab, allowing deeper subduction of the lower units, followed by their uplift through back-folding and/or thrusting of crustal wedges and concomitant exhumation by either erosion or extension (e.g., Escher and Beaumont, 1997; Martinod et al., 2020). In this scenario, the shear zones located between EPMS basement and cover (e.g., Fig. 4.7D), and between EPMS cover and FdLS (e.g., Fig. 4.7A) would have accommodated decoupling during subduction (D1) and subsequent juxtaposition during (D2). Based on the available data, we favor the interpretation in which the EPMS cover and basement remained coupled throughout the Taconic orogenic cycle, with the basement recording a more pronounced amphibolite overprint. However, to determine the stacking sequence of the different crustal slices, further structural studies of the EPMS basement-cover boundary, and the definition of the EPMS basement P-T-t path are needed.

Existing structural and geochronological constraints indicate that the F3 upright folding of recumbent F1 and F2 folds, is linked to widespread amphibolite-facies overprinting that developed in the margin during the Salinic orogenic cycle (e.g., Dallmeyer, 1977; Cawood and Dunning, 1993; Castonguay et al., 2010; Skulski et al., 2015; Willner et al., 2022) (Fig. 4.6d). F3 folding of

the units and the shear zones that bound them suggests that the continental wedges, which decoupled and followed different tectono-metamorphic paths after early D1, were recoupled prior to D3. This, combined with geochronological constraints suggests that D1 and D2 deformation and associated metamorphic overprints developed during the Taconic Orogeny. Structural overprinting relationships suggest that D4 and D5 deformations postdate the Salinic orogeny and are likely related to later, superposed orogenic events, such as the Acadian or Neo-Acadian orogenies.

4.6 Conclusions

This study presents multiscale structural and metamorphic data in the Baie Verte margin. Three tectono-metamorphic units are identified: the East Pond Metamorphic Suite (EPMS) basement, EPMS cover, and the Fleur de Lys Supergroup (FdLS). They are shown to have undergone distinct tectono-metamorphic histories during the Taconic orogenic cycle, involving both subduction and exhumation of the Early Paleozoic Laurentian continental margin. Early D1, occurring between c. 483 and 475 Ma, is marked by high-pressure metamorphism across all units, which is particularly well-preserved in the EPMS cover. Tectonic decoupling of EPMS cover and FdLS occurred during subduction (D1). D2 in the EPMS cover occurred between c. 475 and 452 Ma, and first produced retrograde eclogite facies metamorphism and then progressed to granulite- to amphibolite-facies metamorphism in the EPMS cover. The FdLS was subjected to a Barrovian-style metamorphism characterised by kyanite and staurolite during D2. The coupling of the EPMS cover and FdLS occurred prior to Salinic F3 upright folding along a D2 shear zone, which defines the boundary between the two units. Salinic D3 tectonism was accompanied by amphibolite facies metamorphism and transposition of pre-D3 structures. Later overprinting during D4 and D5, linked

to the Acadian and Neo-Acadian orogenies, suggests continued tectono-metamorphic activity of the Baie Verte margin.

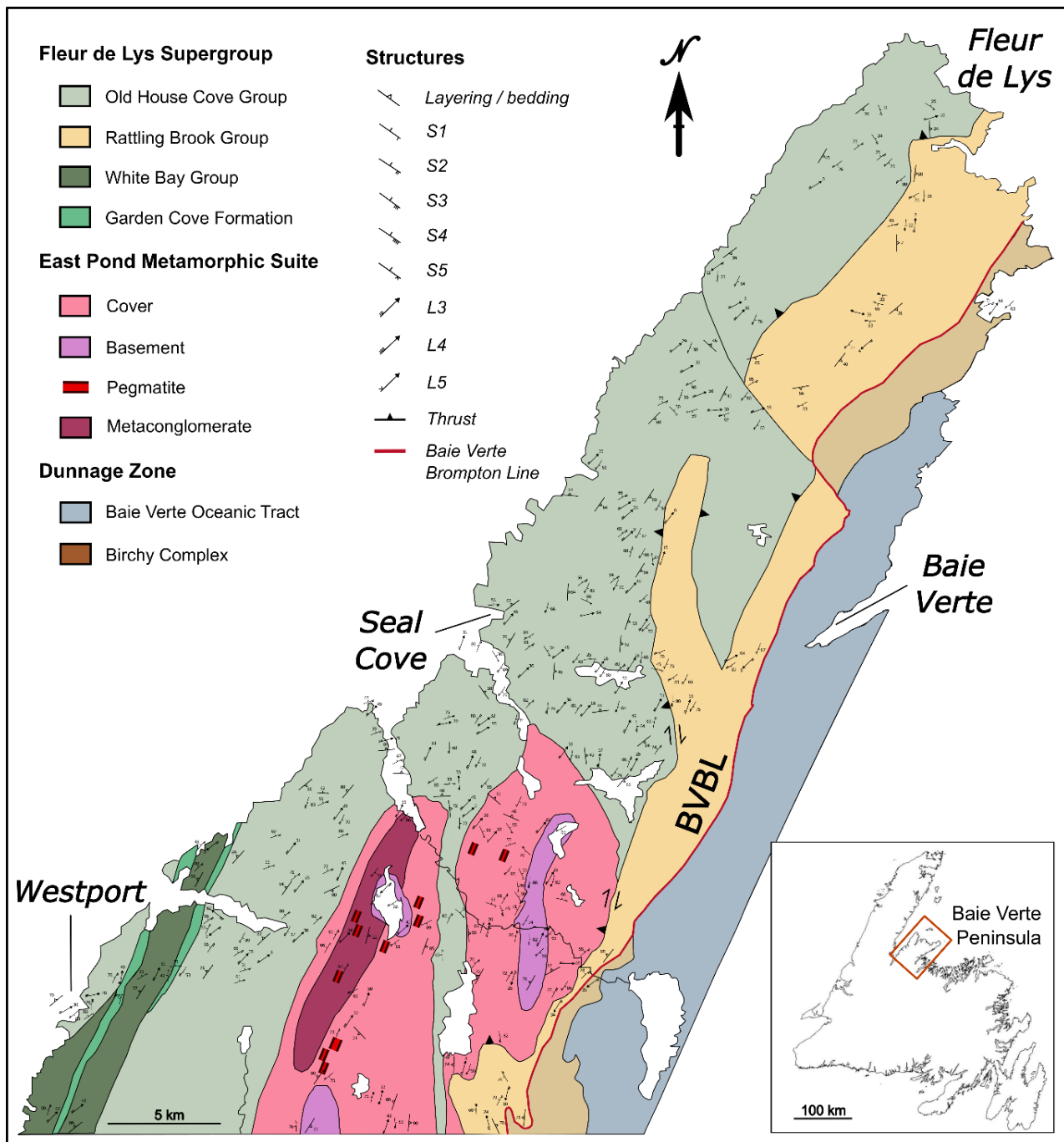


Figure 4.1: Bottom-right inset: Location of the Baie Verte Peninsula within Newfoundland. Main diagram: Summary structural map of the Baie Verte margin. Structural data were collected during this study. The distribution of lithologies and major tectonic lineaments is integrated with

geological maps compiled by the Geological Survey of Canada (Skulski et al., 2017). BVBL: Baie Verte-Brompton Line.

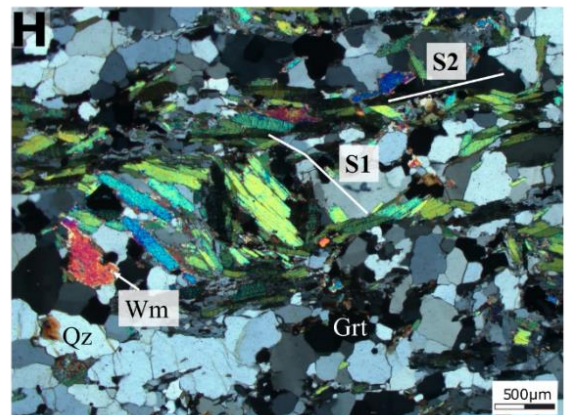
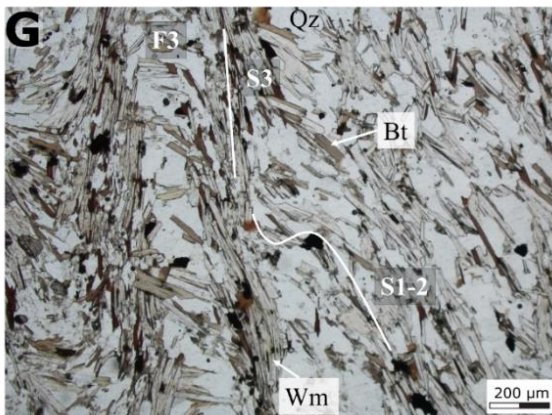
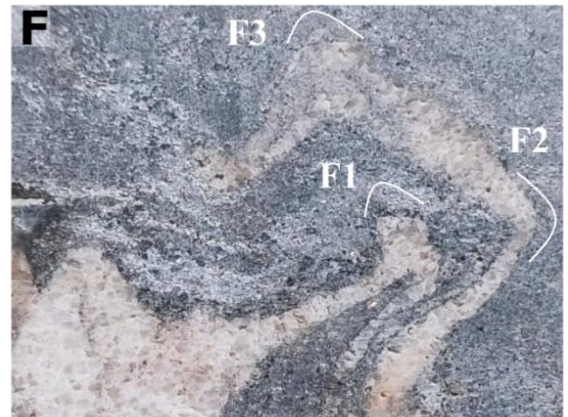
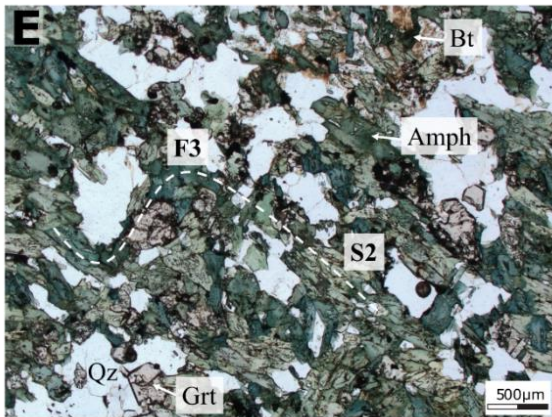
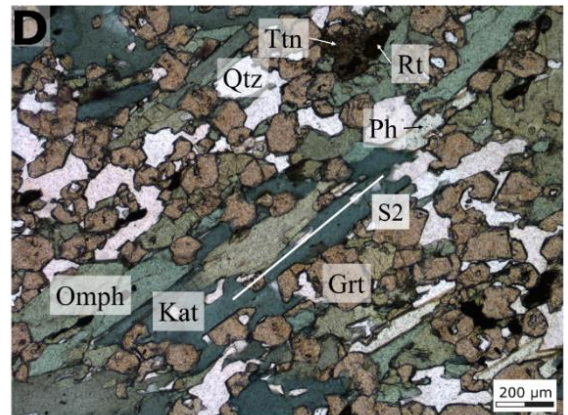
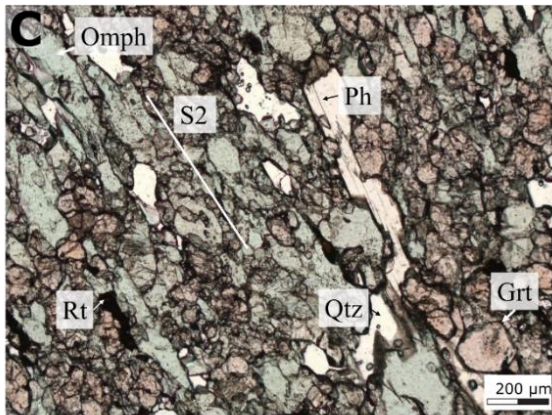


Figure 4.2: (A) Metasediment from the East Pond Metamorphic Suite cover unit, preserving graded bedding and partial Bouma sequences. (B) Eclogite from the East Pond Metamorphic Suite, showing F2 folds with an axial planar S2 foliation defined by garnet-omphacite-rutile-phengite-quartz that, in this case, is sub-parallel to compositional layering (SL). F2 folds the S1 foliation, which is marked by garnet-omphacite-quartz layers. Syn-D3 amphibole veins crosscut the eclogite fabric at a high angle. (C) Microphotograph of well-preserved early S2 eclogite fabric in East Pond Metamorphic Suite mafic pods, characterized by garnet-omphacite-rutile-phengite-quartz. (D) Eclogite from the East Pond Metamorphic Suite where katophorite grows parallel to S2, replacing omphacite. Titanite rims surround rutile, and biotite rims surround phengite grains. (E) Eclogite sampled from the rim of a mafic pod in the East Pond Metamorphic Suite, where pervasive replacement of eclogite minerals is observed. Late S2, marked by katophorite, is folded by F3. (F) Hand sample of metasediment from the East Pond Metamorphic Suite showing the overprinting relationship between F1, F2, and F3 folds. (G) Microphotograph of East Pond Metamorphic Suite metasediment showing F3 folding the composite foliation S1-2, with development of S3 cleavage. (H) S1 foliation highlighted by deformed white mica porphyroblasts, with S2 marked by discontinuous films of white mica.

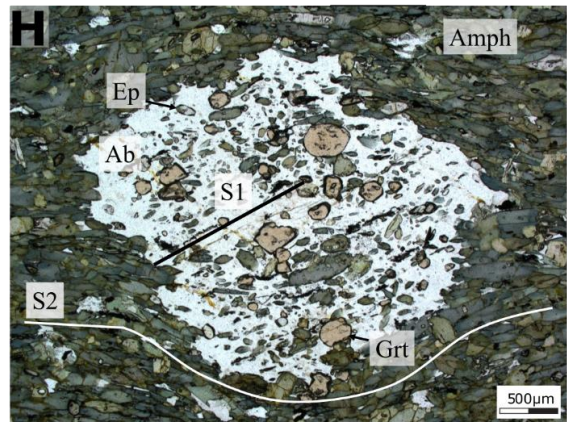
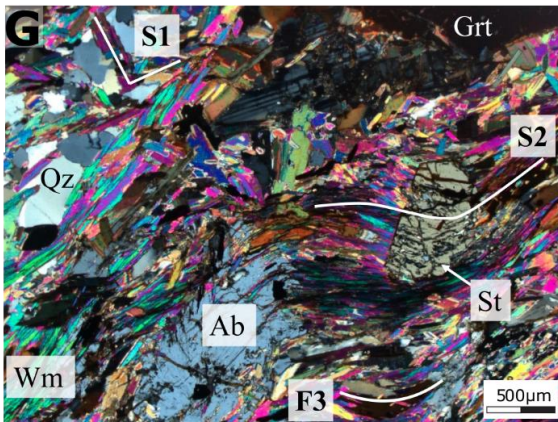
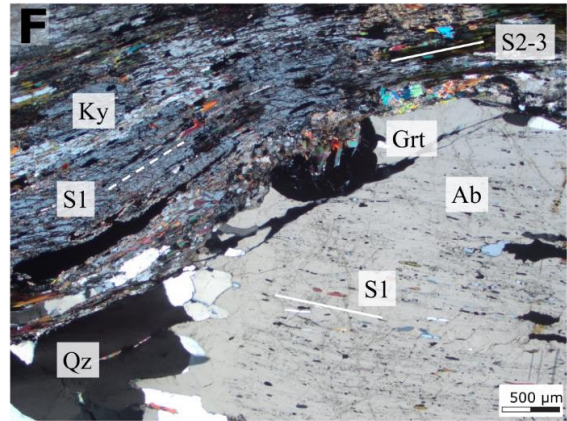
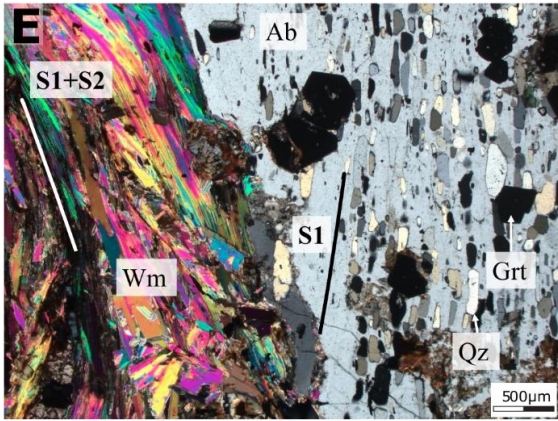
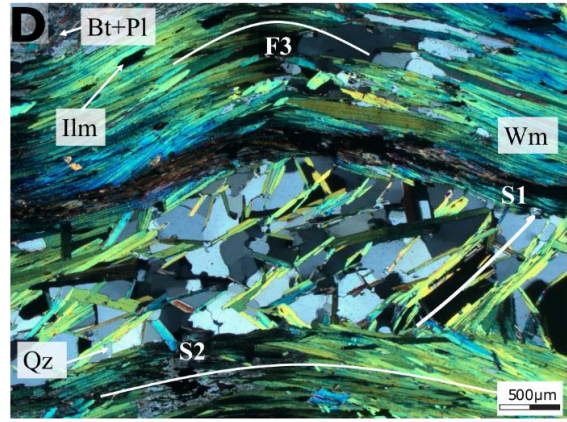
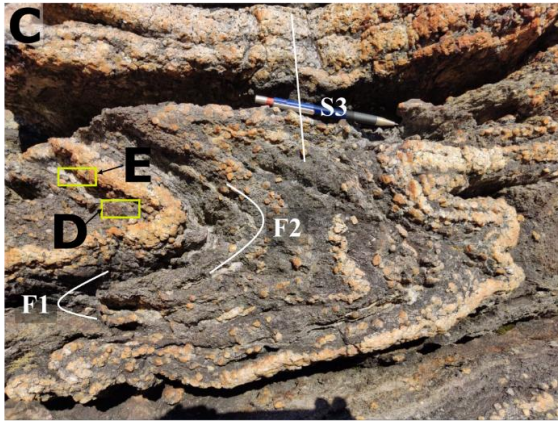
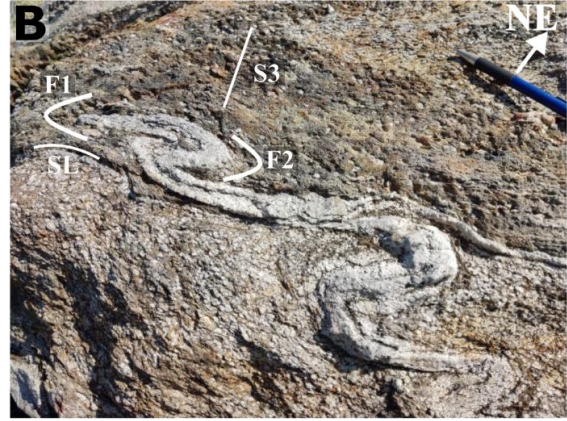
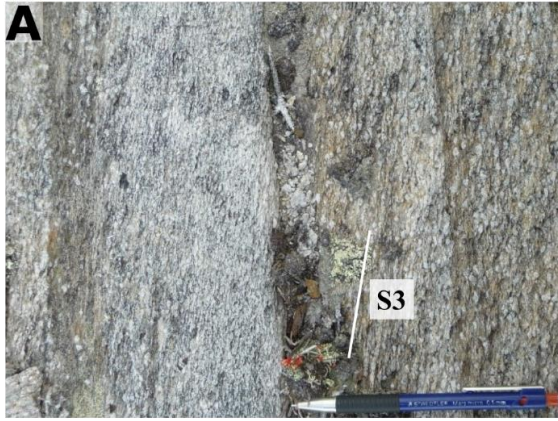


Figure 4.3: (A) Bedding surfaces intersected by S3 foliation in the Fleur de Lys metasediment. (B) Fleur de Lys metasediment preserving two generations of folds (F1 and F2), which are intersected at a high angle by the S3 foliation. (C) Outcrop of Fleur de Lys metasediment located near a regional-scale F3 fold hinge, showing the relationship between pre-D3 structures. F1 folds are re-folded by F2. Albite-porphyroblast-rich layers are folded by F2. Samples collected from this outcrop are indicated by the insets D and E. (D) Fleur de Lys metasediment sampled from the core of the F2 fold shown in (C). The S2 axial planar foliation is marked by mica-rich layers and lithons that preserve a relict S1 foliation. Open F3 folds deform S2. (E) Contact between a micaceous portion and an albite-rich layer sampled near the F2 fold limb in outcrop (C). The albite porphyroblast includes a relict foliation marked by quartz, white mica, and rutile, as well as post-S1 garnets. (F) Microphotograph of a Fleur de Lys metasediment sampled from the tectonic boundary between the Fleur de Lys and East Pond Metamorphic Suite. The albite porphyroblast displays quartz pressure shadows and includes a relict internal S1 foliation oriented at an angle to the external fabric. A garnet grain included within the albite is truncated at the porphyroblast boundary. The composite external foliation (S2-3) wraps around the porphyroblast and is marked by white mica, biotite, and kyanite. Kyanite contains a foliation marked by ilmenite. (G) Microphotograph of a Fleur de Lys metasediment sampled from the northern domain, near the town of Fleur de Lys. The top-left corner shows an S2 lithon with S1 relicts. In the center, an albite porphyroblast is deformed by S2, while a syn-D2 staurolite porphyroblast includes the S2 foliation, marked by oriented quartz, white mica, and ilmenite grains. F3 folds at the bottom of the image deform S2. (H) Microphotograph of a Fleur de Lys mafic boudin where a late D1 albite porphyroblast is enveloped by S2 marked by amphibole.

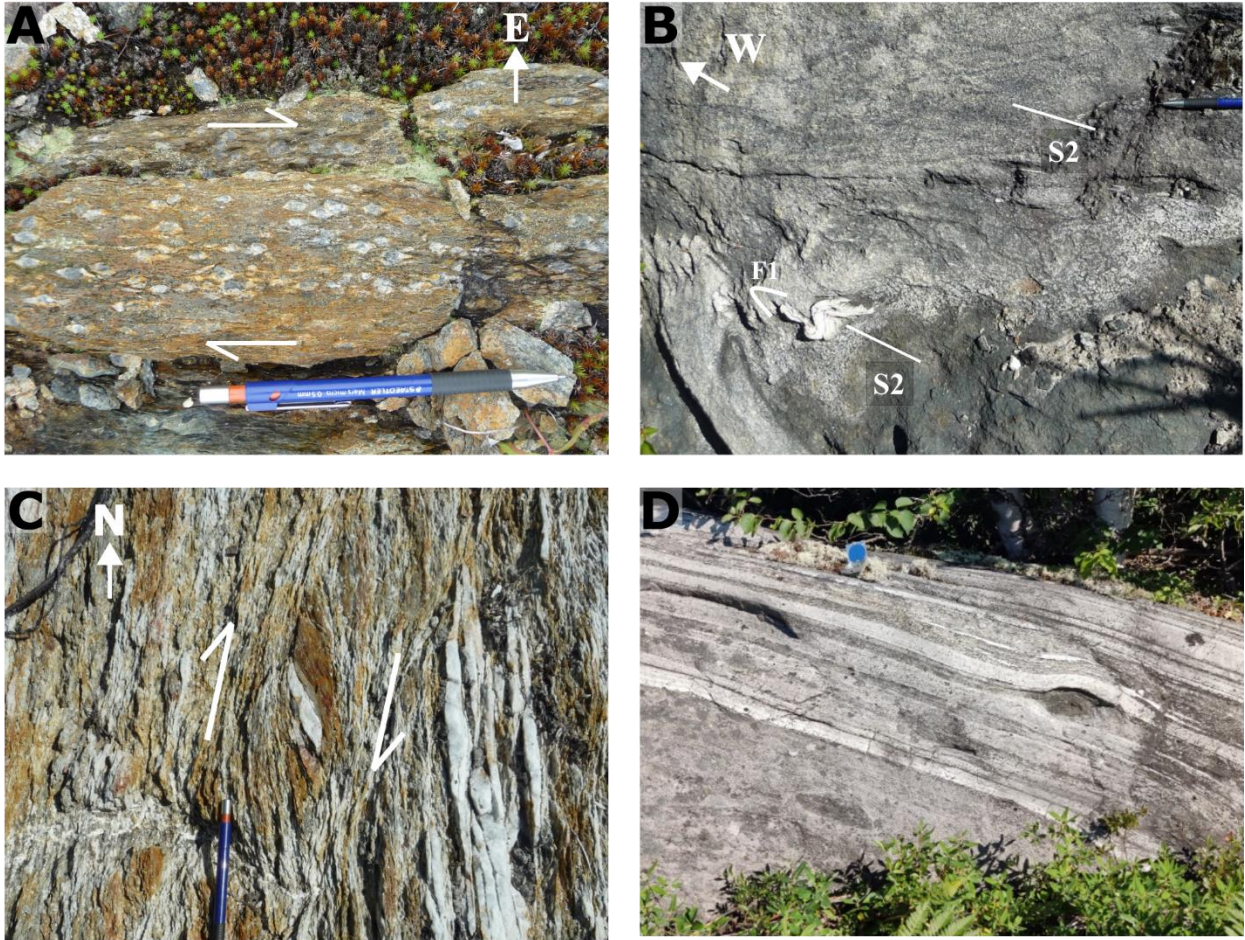


Figure 4.4: (A) Dextral shear sense indicators in albite-porphyroblastic schist at the EPMS cover-FdLS boundary. (B) Westward direction of transport of F2 folds in a deformed psammite in the EPMS. A quartz vein highlights F1 isoclinal fold refolded by F2. (C) Reverse, top to the E kinematic of the shear zone at the contact between the EPMS cover and Rattling Brook Group (the outcrop surface is sub-vertical). (D) Mylonite occurs between the basement and cover in the EPMS.

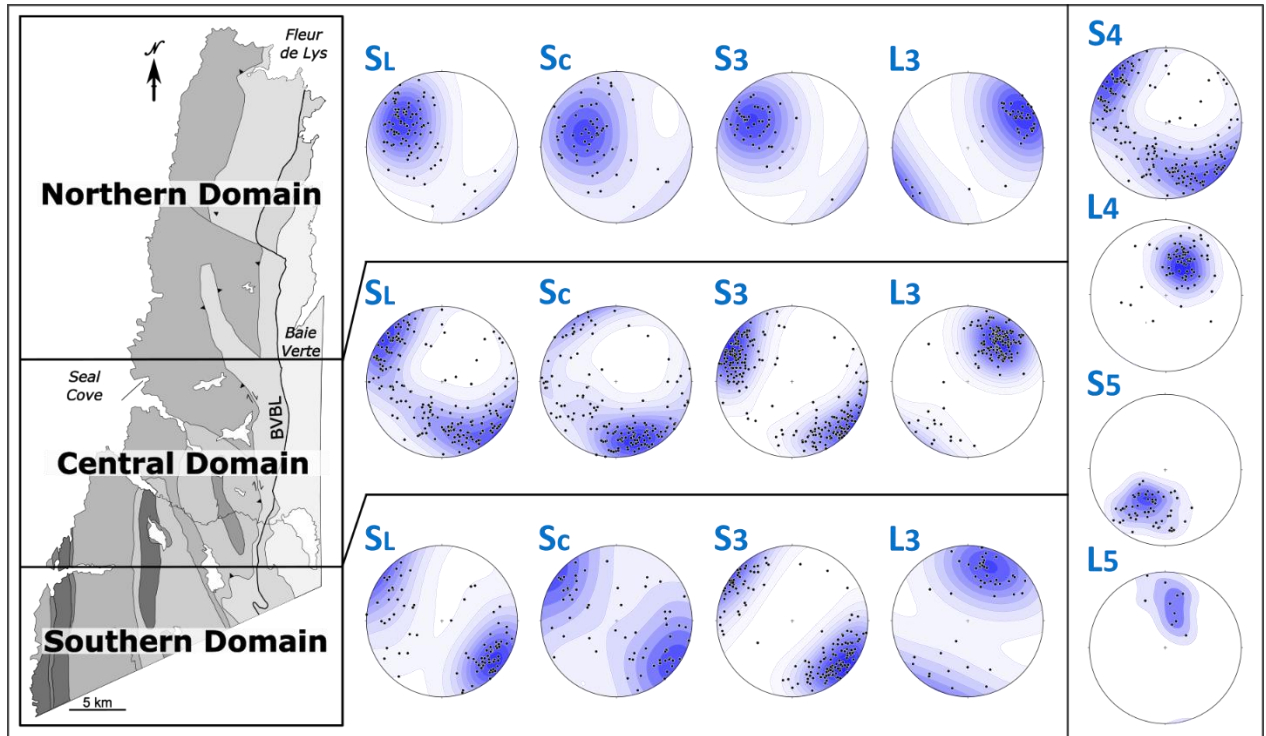


Figure 4.5: Left: Summary diagram of structural domains. Center: Equal-area, lower-hemisphere stereonets displaying structural measurements from each structural domain. Right: Stereonet of structures that did not exhibit significant variations across the different structural domains. All orientation data were collected during this study. Stereographic projections were generated using Stereonet v.11 (Allmendinger et al., 2011; Cardozo and Allmendinger, 2013). S_L : Bedding (or layering in the East Pond Metamorphic Suite basement); S_c : Composite foliation of S_L , S_1 , and S_2 ; $S_{(n)}$: Axial planar foliations associated with successive deformation stages; $L_{(n)}$: Mineral lineations and folds axes related to successive folding stages.

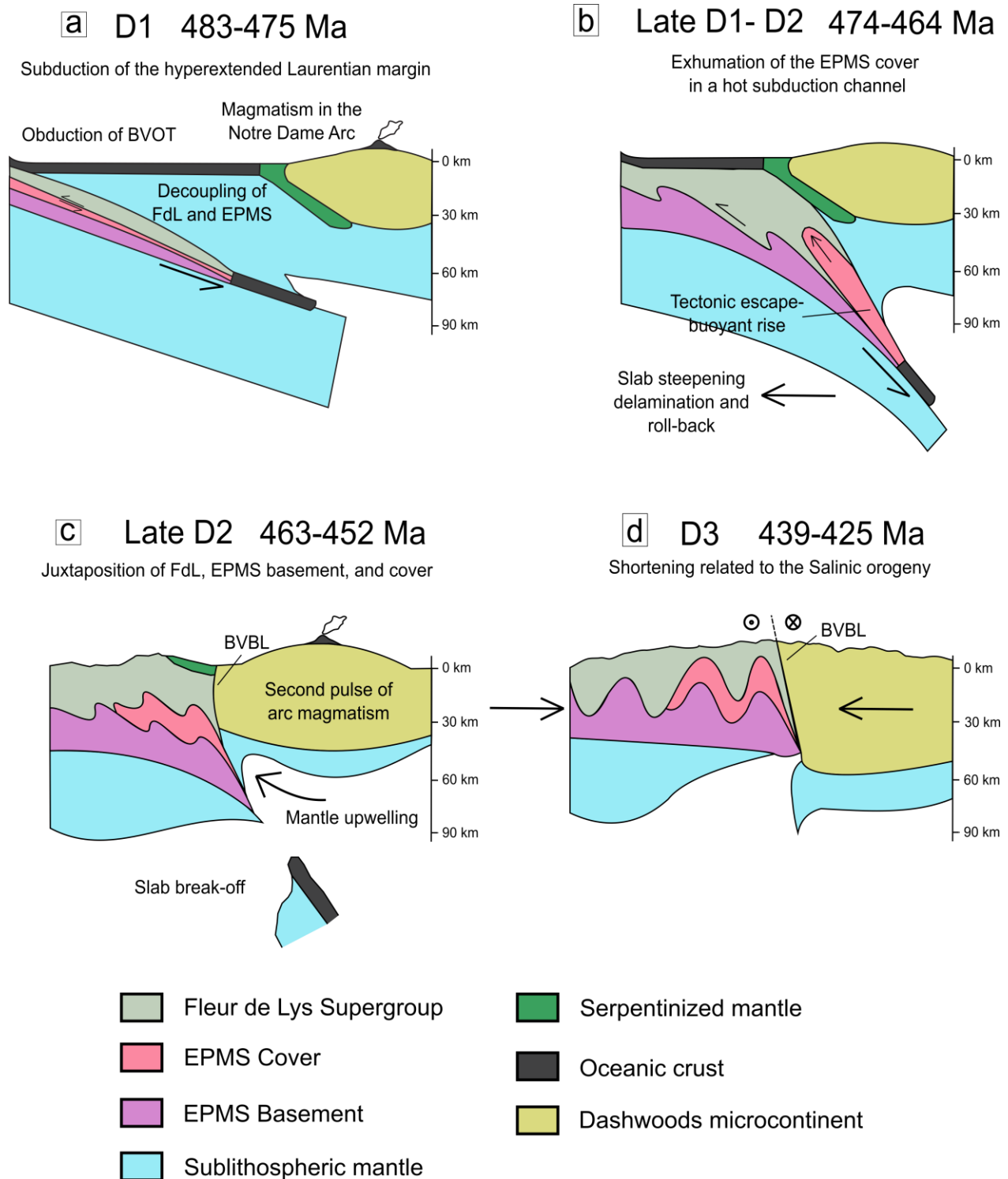


Figure 4.6: Model for the evolution of the Baie Verte margin since Early Paleozoic time. a) Subduction of the hyperextended Baie Verte continental margin. b) Exhumation of the subducted continental units initiates at the subduction-collision transition. Exhumation is initially facilitated by buoyant rise of the continental wedges in a rheologically weak metasedimentary channel and is

triggered by slab steepening and/or slab roll back. c) Following slab break-off, further exhumation is accommodated by extension and erosion, tectonic coupling of the continental wedges occurs along D2 shear zones. d) Shortening related to collisional tectonics during the Salinic orogeny generates regional scale upright folding in the exhumed continental pile. See text for further discussion. EPMS: East Pond Metamorphic Suite; FdLS: Fleur de Lys Supergroup; BVBL; Baie Verte-Brompton Line; BVOT; Baie Verte Oceanic Tract.

Chapter 5: Summary and Conclusions

5.1 Main Conclusions

5.1.2 Tectono-Stratigraphy and Regional Structure of the Baie Verte Margin (Chapter 4)

- The Baie Verte margin consists of three tectono-metamorphic units: the East Pond Metamorphic Suite (EPMS) basement, comprising Mesoproterozoic Grenvillian basement rocks; the EPMS cover, dominated by quartzofeldspathic metasediments with mafic boudins and metavolcanic rocks; and the Fleur de Lys Supergroup (FdLS), which mainly consists of psammitic and pelitic metasedimentary cover rocks with mafic boudins.
- The overall structural architecture of the Baie Verte margin is defined by regional-scale, upright, northeast-trending F3 folds, which deform earlier structures in the tectono-metamorphic units and the shear zones that bound them. The deepest structural levels are exposed in the cores of F3 antiforms, which are separated by tight synforms cored by the Fleur de Lys Supergroup (FdLS).

5.1.3 Tectono-Metamorphic Evolution (Chapters 2 and 3)

- The earliest deformation event, D1, is associated with medium- to high-pressure metamorphism that occurred across all units. In the EPMS cover, this stage is associated with the attainment of eclogite-facies conditions of ~2.8 GPa, 620°C at 483–475 Ma.
- During late D1, the EPMS cover, possibly coupled with the basement, was subducted to peak pressure conditions, while the EPMS FdLS was exhumed to crustal levels (Fig. 4.6a).
- Exhumation of the EPMS cover occurred during D2 and resulted in retrograde metamorphism, progressing from eclogite- to granulite- to amphibolite-facies between 475–452 Ma. Barrovian metamorphism occurred during D2 in the FdLS, which is

characterised by kyanite and staurolite growth. Coupling between the EPMS cover and FdLS is inferred to have occurred via the D2 shear zone at the EPMS cover-FdLS interface before the onset of D3 folding (Fig. 4.6b, c).

- F3 folding and transposition of pre-existing structures along the F3 limbs occurred under amphibolite-facies conditions during the Salinic orogenic cycle between c. 439–425 Ma (Fig. 4.6d).
- D4 and D5 are associated with tectono-metamorphic activity that occurred during the Acadian and Neo-Acadian orogenies.

5.1.4 Subduction and Exhumation of the EPMS Eclogites (Chapter 2)

The eclogites of the East Pond Metamorphic Suite (EPMS) reached peak metamorphic conditions of approximately 2.8 GPa and 620°C, overlapping with ultrahigh-pressure (UHP) conditions near the coesite stability field (~75 km depth). During decompression, these rocks recorded a β -shaped P-T path that suggests a multi-stage exhumation process. The first stage involved near-isothermal decompression from peak pressures of ~2.8 GPa and 620°C to ~2 GPa and 660°C, which is interpreted to result from buoyancy-driven vertical extrusion from mantle to crustal depths. This process likely occurred within a low-viscosity deformation channel, bounded by a basal thrust-sense shear zone and an upper normal-sense shear zone. In the second stage, the rocks experienced heating to ~860°C at 1.5 GPa, possibly due to mantle upwelling associated with slab rollback or break-off. This event further facilitated the exhumation of the EPMS via a hot inter-plate exhumation channel. Finally, the third stage was marked by continued decompression, cooling, and significant fluid influx, which promoted retrograde metamorphic reactions. These reactions initially produced katophorite-bearing amphibolite assemblages and later formed pargasite, biotite, and plagioclase. During this final stage, exhumation likely slowed and was driven by external

forces, such as displacement along shear zones, erosional unroofing, or extensional tectonics, which localized deformation and fluid access within crustal shear zones rather than in a rheologically weak mantle channel.

5.1.5 Tectonic Model and Implications for Exhumation Mechanisms (Chapter 4)

The three metamorphic units of the Baie Verte margin recorded similar P–T conditions during the early stages of D1. However, available data indicate that at least the East Pond Metamorphic Suite (EPMS) and the Fleur de Lys Supergroup (FLDS) were subducted to different depths, suggesting that tectonic decoupling occurred during subduction. By the late D2 stage, the similarities in the metamorphic record across the three units indicate that they had been juxtaposed prior to the onset of D3.

Based on current data, two possible tectonic models can explain the evolution of the Baie Verte margin during Taconic subduction and exhumation. In the first model, the detached EPMS basement and cover were emplaced beneath the FLDS during exhumation along the D2 shear zone, with melt weakening facilitating this movement. In the second model, the three units detached sequentially from the top of the subducting slab and were subsequently juxtaposed and stacked through back-thrusting.

This research on the Baie Verte margin serves as a case study illustrating how the integration of field observations, petrographic analysis, petrochronology, and thermodynamic modeling can provide valuable insights into the processes associated with deep subduction and exhumation of continental margins. Furthermore, the detailed reconstruction of the tectono-metamorphic stages

recorded by the eclogites has enhanced our understanding of the evolution of high-pressure to ultrahigh-pressure (HP-UHP) units, particularly those that experienced significant high-temperature overprinting during exhumation.

5.2 Future Directions

Several research directions could further enhance our understanding of the tectonic evolution of the Baie Verte margin and provide insights into the mechanisms that control the geodynamic evolution of subduction systems in general.

Field mapping was a fundamental aspect of this research (Chapter 4). While many key areas inland have been thoroughly surveyed, additional structural mapping and sampling along the northern coastline of the Peninsula would help define the regional structural framework of this part of the margin. Further fieldwork should also explore the possibility of fresh eclogite occurrences within the EPMS basement to determine if this unit ever recorded eclogite facies conditions. Finally, to unravel the relative timing of the decoupling and recoupling processes between the EPMS basement and cover, additional work should focus on reconstructing the kinematics at their interface.

The timing of D1 and D2 has been defined in this study exclusively for the EPMS cover in Chapter 3. Determining the absolute ages of these events in other units would better constrain their tectonic evolution, with important implications for the duration of deformation, metamorphism, and the processes of decoupling and juxtaposition of continental wedges in subduction systems.

The occurrence of migmatites in the EPMS basement, in proximity to late Taconic pegmatites and leucosome in the EPMS cover, raises the question of whether these features are linked to the Taconic Orogenic cycle or to Proterozoic magmatic events recognized in the basement. Further

Zircon U-Pb geochronological investigations of the basement migmatites would test whether both the basement and cover experienced a late Taconic thermal perturbation, with significant implications for understanding the timing of their decoupling and juxtaposition.

While this study improves our understanding of the relationship between deformation events and albite porphyroblast growth in the Fleur de Lys Supergroup (FdLS) (Chapter 4), outstanding questions remain about their occurrence in exhumed (U)HP terranes (e.g., Mposkos and Krohe 2000; Papeschi et al., 2020). Detailed P–T work on the Fleur de Lys metasediments and associated mafic pods could help assess their relationship to retrograde metamorphism and the role of metasomatism in controlling albite porphyroblast growth.

This study did not include an investigation of the Rattling Brook Group. Further work in this unit, aimed at clarifying its relationship with the evolution of adjacent units, could lead to the identification of a new tectono-metamorphic unit within the Early Paleozoic Laurentian margin, providing insights into the mechanisms responsible for the juxtaposition of continental wedges in subduction-collision orogens.

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Appendices

Appendix A1: Analytical Methods

Table A1 – I: Summarized methods for EPMA and LA-ICPMS analysis.

EPMA										
Model	JEOL JXA-8230 Superprobe									
Voltage	15 kV									
Amphibole										
Current	100 nA									
Spot size	1µm									
	F	Mn	Fe	K	Ca	Na	Al	Si	Mg	Ti
Peak counting time (s)	10	30	30	20	30	20	30	20	30	30
Background counting time (s)	5	15	15	10	15	10	15	10	15	15
Element X-ray line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Analyzing crystal	LDE1	LIFL	LIFL	PETL	PETL	TAP	TAP	TAP	TAP	LIFH
Primary Standard	JMH_fluorapatite_319	Rhodenite	Almandine_Garnet	Orthoclase	Diopside	Albite	Almandine_Garnet	Diopside	Diopside	rutile
Garnet										
Current	200 nA									
Spot size	1µm									
	Mn	Fe	Ca	Na	Al	Si	Mg	Ti	Cr	
Peak counting time (s)	30	30	30	20	30	20	30	30	30	30
Background counting time (s)	15	15	15	10	15	10	15	15	15	15
Element X-ray line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	
Analyzing crystal	LIFL	LIFL	PETL	TAP	TAP	TAP	TAP	LIFH	LIFH	
Primary Standard	Rhodenite	Almandine_Garnet	Diopside	AmeliaAlbite	pyrope	Diopside	Diopside	rutile	Chromium_Oxide	

Table A1 – I: (continued)

Clinopyroxene										
Current	199 nA									
Spot size	3 µm									
	Mn	Fe	K	Ca	Na	Al	Si	Mg	Ti	Cr
Peak counting time (s)	30	30	20	30	20	30	20	30	30	30
Background counting time (s)	15	15	10	15	10	15	10	15	15	15
Element X-ray line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Analyzing crystal	LIFL	LIFL	PETL	PETL	TAP	TAP	TAP	TAP	LIFH	LIFH
Primary Standard	Rhodenite	Almandine_Garnet	Orthoclase	Diopside	AmeliaAlbite	Almandine_Garnet	Diopside	Diopside	rutile	Chromium_Oxide
White mica										
Current	200 nA									
Spot size	3 µm									
	F	Mn	Fe	K	Ca	Na	Al	Si	Mg	Ti
Peak counting time (s)	10	30	30	20	30	20	30	20	30	30
Background counting time (s)	5	15	15	10	15	10	15	10	15	15
Element X-ray line	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα	Kα
Analyzing crystal	LDE1	LIFL	LIFL	PETL	PETL	TAP	TAP	TAP	TAP	LIFH
Primary Standard	JMH_fluorapatite_319	Rhodenite	Almandine_Garnet	Orthoclase	Diopside	AmeliaAlbite	Almandine_Garnet	Diopside	Diopside	rutile
Rutile										
Current	200 nA									
Spot size	2 µm									
	Fe	Ti	Nb							
Peak counting time (s)	30	10	30							
Background counting time (s)	15	2	15							
Element X-ray line	Kα	Kα	Lα							
Analyzing crystal	LIFL	LIFH	PETL							
Primary Standard	Magnetite	rutile	Nb							

Table A1 – I: (continued)

Titanite						
Current	100 nA					
Spot size	2µm					
	F	Fe	Ca	Al	Si	Ti
Peak counting time (s)	10	30	30	30	20	30
Background counting time (s)	5	15	15	15	10	15
Element X-ray line	Kα	Kα	Kα	Kα	Kα	Kα
Analyzing crystal	LDE1	LIFL	PETL	TAP	TAP	LIFH
Primary Standard	JMH_fluorapatite_319	Almandine_Garnet	Diopside	Almandine_Garnet	Diopside	rutile
Apatite						
Current	200 nA					
Spot size	10µm					
	F	P	Cl	Ca		
Peak counting time (s)	10	20	20	30		
Background counting time (s)	5	10	10	15		
Element X-ray line	Kα	Kα	Kα	Kα		
Analyzing crystal	LDE1	PETL	PETL	PETL		
Primary Standard	JMH_fluorapatite_319	Apatite	JMH_chlorapatite_346	Diopside		
LA-ICP-MS						
Model	Thermo-Finnigan ELEMENT XR coupled with a GeoLas 193 nm Excimer laser system					
Pulse frequency	5 Hz					
Energy density	4 J/cm ²					
Spot size	40 µ					
Gas blank	30s					
Signal	60s					
Titanite internal standard	Ca (from EPMA)					
Apatite internal standard	Ca (from EPMA)					
Internal standard	Ti (from EPMA)					
Primary reference material	NIST-610					
Secondary reference material	BCR-2G					

Appendix A2: Samples Location

Table A2: GPS coordinates of the analyzed samples.

	Latitude	Longitude	UTM E	UTM N
93LS1a/c	49.796796	-56.359306	546109.8	5516235
149LS1	49.851221	-56.391161	543768.1	5522267
152LS1	49.851505	-56.392033	543705.1	5522298
182LS1	49.786074	-56.477917	537581.8	5514977
183LS1	49.786074	-56.477917	537581.8	5514977
230LS1	49.786074	-56.477917	537581.8	5514977
312LS2	49.856410	-56.390300	543825.3	5522844

Appendix A3: Whole Rock Geochemistry

Table A3 – I: Eclogites whole rock geochemistry.

Analyte Symbol	Unit Symbol	Detection Limit	Analysis Method	93LS1a	93LS1c	187LS1	152LS1
Co3O4	%	0.005	FUS-XRF	0.007	0.007	0.009	0.007
CuO	%	0.005	FUS-XRF	0.024	< 0.005	0.015	< 0.005
NiO	%	0.003	FUS-XRF	0.035	0.003	0.017	0.004
SiO2	%	0.01	FUS-XRF	49.15	48.27	48.81	49.65
Al2O3	%	0.01	FUS-XRF	12.00	12.40	12.87	13.28
Fe2O3(T)	%	0.01	FUS-XRF	18.72	18.84	15.19	16.14
MnO	%	0.005	FUS-XRF	0.283	0.285	0.224	0.240
MgO	%	0.01	FUS-XRF	5.15	5.10	6.44	6.22
CaO	%	0.01	FUS-XRF	9.48	9.18	11.58	10.50
Na2O	%	0.01	FUS-XRF	2.30	2.31	2.29	2.42
K2O	%	0.01	FUS-XRF	0.28	0.30	0.30	0.20
TiO2	%	0.01	FUS-XRF	2.57	2.54	1.82	1.92
P2O5	%	0.01	FUS-XRF	0.28	0.25	0.21	0.19
Cr2O3	%	0.01	FUS-XRF	0.03	0.01	0.02	0.01
V2O5	%	0.003	FUS-XRF	0.097	0.092	0.086	0.086
LOI	%		GRAV	-0.44	-0.73	-0.45	-0.39
LOI2	%		FUS-XRF	1.11	0.72	0.84	1.24
Total	%	0.01	FUS-XRF	99.98	98.84	99.43	100.50
Total2	%	0.01	FUS-XRF	> 101	100	101	102
Fe2O3	%	0.01	FUS-XRF	3.36	4.39	2.38	< 0.01
FeO	%	0.1	TITR	13.8	13.0	11.5	14.5

Table A3 – II: Whole rock compositions expressed in wt % oxide obtained from XRF analyses of samples used for thermodynamic modelling. Abbreviations: FUS-XRF, Lithium borate fusion with X-Ray Fluorescence analysis; GRAV, gravimetric; TITR, titration.

	SiO ₂	Al ₂ O ₃	MgO	Fe ₂ O ₃	FeO	CaO	K ₂ O	Na ₂ O	TiO ₂	LOI	Total
93LS1a	49.15	12.00	5.15	3.36	13.80	9.48	0.28	2.30	0.28	2.57	99.98
93LS1c	48.27	12.40	5.10	4.39	13.00	9.18	0.30	2.31	0.30	2.54	98.84

Appendix A4: Mineral Chemistry

Table A4 – I: Representative compositions of the main amphibole generations identified in the samples analyzed.

Mineral Sample	Katophorite 93LS1a	Sadanagaite 93LS1c In contact with Grt	Pargasite 2 183LS1	Pargasite 1 93LS1a	Hornblende 183LS1	Actinolite 183LS1
Location	Matrix		Matrix	Vein	Matrix	Matrix
(Wt %)						
SiO ₂	46.78	36.92	40.50	42.53	45.92	51.98
TiO ₂	0.40	0.08	0.68	0.55	0.29	0.03
Al ₂ O ₃	11.26	19.48	11.48	11.44	7.19	2.28
MnO	0.03	0.36	0.38	0.21	0.38	0.38
FeO	13.45	20.04	16.68	19.41	14.19	12.57
Fe ₂ O ₃	1.93	2.84	3.81	1.95	3.26	1.52
MgO	10.36	3.78	7.83	7.41	11.02	14.39
CaO	7.57	9.95	11.32	9.74	11.48	11.80
Na ₂ O	3.88	3.26	1.49	2.87	1.00	0.43
K ₂ O	0.49	0.08	1.26	0.84	0.56	0.16
H ₂ O+	2.02	1.93	1.92	1.95	1.97	2.02
Total	98.18	98.71	97.35	98.89	97.26	97.56
(A.p.f.u.)						
Na(A)	0.44	0.80	0.40	0.59	0.23	0.36
Na(B)	0.67	0.17	0.05	0.27	0.07	0.07
Ca(B)	1.20	1.66	1.90	1.60	1.87	1.87
Al ^{IV}	1.06	2.26	1.66	1.46	1.00	0.30

A.p.f.u. and H₂O+ values were calculated following the IMA2012 recommendations using the spreadsheet developed by Locock, (2014), (Science direct page: <https://www.sciencedirect.com/science/article/pii/S0098300413002513?via%3Dihub#ec0005>).

Table A4 – II: Representative EPMA compositions of garnet zones in sample 93LS1a.

Wt %	Core	Mantle 1	Mantle 2	Rim 3
SiO ₂	37.63	37.49	37.78	37.59
TiO ₂	0.16	0.05	0.03	0.06
Al ₂ O ₃	21.02	21.67	21.94	21.57
Cr ₂ O ₃	0.01	0.00	0.00	0.00
FeO	27.41	32.32	30.58	29.07
MnO	0.54	0.98	0.79	0.79
MgO	3.55	3.15	3.33	4.66
CaO	9.81	4.99	6.34	5.46
Total	100.23	100.65	100.79	99.20
Mol %				
Spessartine	1.2	2.2	1.8	1.8
Pyrope	13.9	12.4	13.0	18.4
Almandine	56.4	70.4	66.5	63.9
Grossular	24.0	14.0	17.8	15.3
Andradite	3.1	0.0	0.0	0.0

Table A4 – III: Amphibole chemistry.

	F wt%	MnO wt%	FeO wt%	K ₂ O wt%	CaO wt%	Na ₂ O wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	MgO wt%	TiO ₂ wt%	Total wt%
93LS1a											
93LS1a-1-3	L.O.D.	0.35	9.26	2.65	8.26	46.25	9.39	19.60	0.20	0.46	96.17
93LS1a-1-4	L.O.D.	0.56	7.71	3.80	10.99	47.21	10.56	15.26	0.08	0.42	96.28
93LS1a-1-5	L.O.D.	0.51	7.70	3.50	9.94	48.11	11.07	14.78	0.05	0.37	95.74
93LS1a-1-5.5	L.O.D.	0.29	8.52	2.84	8.07	47.04	9.23	19.37	0.25	0.61	95.99
93LS1a-1-6	L.O.D.	0.84	9.74	2.87	11.44	42.53	7.41	21.16	0.21	0.55	96.45
93LS1a-1-7	L.O.D.	0.33	8.55	2.83	7.84	46.27	8.84	20.44	0.29	0.60	95.72
93LS1a-1-9	L.O.D.	0.44	9.57	2.45	8.83	46.28	8.80	19.96	0.23	0.30	96.62
93LS1a-2-7	L.O.D.	0.57	7.73	3.78	11.93	45.64	9.28	16.50	0.08	0.44	95.63
93LS1a-2-8	L.O.D.	0.64	8.01	3.56	12.79	45.22	9.49	15.89	0.08	0.41	95.73
93LS1a-2-9	L.O.D.	0.32	8.99	2.63	7.29	47.49	9.64	19.57	0.27	0.45	96.41
93LS1a-3-1	L.O.D.	0.63	7.86	3.99	12.56	45.32	9.55	15.77	0.02	0.50	95.89
93LS1a-3-2	L.O.D.	0.62	7.93	3.97	12.19	45.77	9.65	15.64	0.05	0.44	95.95
93LS1a-3-3	L.O.D.	0.53	7.85	3.72	10.52	47.62	10.67	14.97	0.03	0.38	96.01
93LS1a-3-4	L.O.D.	0.59	7.81	3.85	10.71	47.27	10.76	14.83	0.04	0.40	95.97
93LS1a-4-1	L.O.D.	0.63	7.90	3.90	12.80	45.49	9.59	15.41	0.05	0.46	95.91
93LS1a-4-2	L.O.D.	0.61	8.32	3.38	9.81	47.49	11.33	14.93	0.02	0.32	95.95
93LS1a-4-3	L.O.D.	0.49	7.57	3.88	11.26	46.78	10.36	15.19	0.03	0.40	95.65
93LS1c											
93LS1c-4-5	L.O.D.	0.19	21.72	8.03	1.51	0.13	13.29	37.43	9.22	1.46	92.70
93LS1c-4-4	L.O.D.	0.20	16.23	0.45	11.90	1.13	6.70	47.38	12.06	0.17	95.88
93LS1c-4-3	L.O.D.	0.18	14.01	0.25	11.93	1.02	6.21	49.47	13.61	0.19	96.54
93LS1c-4-2	L.O.D.	0.18	14.09	0.22	11.94	1.12	6.51	48.96	13.33	0.27	96.28
93LS1c-4-1	L.O.D.	0.18	12.63	0.16	12.29	0.67	4.51	51.14	14.97	0.20	96.42
93LS1c-3-1	L.O.D.	0.06	16.79	0.68	7.98	3.99	13.75	44.16	8.75	0.47	96.36
93LS1c-3-2	L.O.D.	0.03	16.35	0.61	7.75	3.88	12.32	45.93	9.45	0.48	96.92
93LS1c-2-4	L.O.D.	0.18	14.21	0.15	11.81	0.84	5.57	49.52	13.00	0.17	95.10
93LS1c-1-5	L.O.D.	0.04	15.14	0.52	7.89	3.58	9.61	48.27	11.05	0.35	96.17
93LS1c-1-4	L.O.D.	0.29	20.36	0.06	9.72	3.40	20.96	37.02	4.63	0.06	96.27
93LS1c-5-2	L.O.D.	0.13	18.42	0.71	8.25	3.56	14.00	43.42	7.56	0.42	96.24
93LS1c-5-3	L.O.D.	0.06	15.48	0.63	8.33	3.45	9.49	47.48	10.90	0.28	95.80
93LS1c-5-4	L.O.D.	0.10	18.61	0.59	8.87	3.16	12.67	44.08	7.98	0.57	96.37
93LS1c-5-1	L.O.D.	0.01	16.03	0.56	7.90	4.10	11.56	46.18	9.81	0.42	96.72
93LS1c-6-11	L.O.D.	0.03	16.63	0.51	8.02	3.77	12.03	45.91	9.39	0.42	96.46
93LS1c-6-12	L.O.D.	0.09	15.54	0.03	11.99	0.65	3.74	51.09	12.96	0.14	95.87
93LS1c-6-16	L.O.D.	0.03	15.93	0.60	8.08	3.64	10.41	47.34	10.43	0.34	96.52
93LS1c-6-15	L.O.D.	0.36	22.59	0.08	9.95	3.26	19.48	36.92	3.78	0.08	96.29
93LS1c-6-16	L.O.D.	0.08	16.66	0.63	8.06	3.86	12.15	45.31	9.31	0.49	96.29
93LS1c-6-17	L.O.D.	0.05	15.82	0.57	7.32	3.95	11.11	47.00	9.77	0.43	95.75
152LS1											
152LS1-5-2	L.O.D.	0.02	10.60	0.67	9.35	3.63	12.57	46.81	13.47	0.39	97.30
152LS1-5-1	L.O.D.	0.04	10.29	0.56	9.03	3.48	12.04	47.31	13.58	0.32	96.41
152LS1-2-11	L.O.D.	0.02	10.10	0.56	9.02	3.30	10.92	47.23	13.43	0.52	94.78
152LS1-2-12	L.O.D.	0.01	6.66	0.00	15.02	6.22	8.39	54.73	9.23	0.09	100.10
152LS1-1-2	L.O.D.	0.03	12.54	0.85	9.30	3.79	15.23	43.84	11.55	0.50	97.33
152LS1-1-1	L.O.D.	0.16	15.41	0.55	10.58	3.10	14.80	42.39	9.57	0.57	96.90
152LS1-1-4	L.O.D.	0.14	16.97	0.86	11.28	1.98	11.30	43.29	9.92	0.75	96.19
152LS1-1-5	L.O.D.	0.08	12.07	0.80	9.48	3.30	13.70	45.11	11.80	0.40	96.43
152LS1-6-1	L.O.D.	0.03	9.57	0.69	9.26	3.14	10.98	48.53	14.25	0.29	96.80
152LS1-6-2	L.O.D.	0.02	9.74	0.54	9.02	3.76	11.53	47.63	13.80	0.29	96.11
152LS1-8-4	L.O.D.	0.37	18.37	0.12	11.32	0.80	3.48	51.00	11.41	0.20	96.71
152LS1-8-3	L.O.D.	0.32	18.05	0.13	12.39	0.64	2.58	50.74	11.23	0.18	95.88
152LS1-8-2	L.O.D.	0.29	18.11	0.14	11.55	0.84	3.56	50.46	11.16	0.27	96.06
152LS1-9-1	L.O.D.	0.03	11.13	0.59	9.51	3.66	15.31	45.17	11.95	0.38	97.52
152LS1-9-2	L.O.D.	0.32	17.40	0.08	11.99	0.54	2.39	51.98	12.13	0.14	96.65
152LS1-10-14	L.O.D.	0.03	10.43	0.58	9.22	3.61	12.56	46.84	13.34	0.37	96.77
152LS1-10-15	L.O.D.	0.05	6.61	0.01	14.87	6.34	8.53	54.93	9.32	0.03	100.41

Table A4 – III: (Continued)

	F wt%	MnO wt%	FeO wt%	K ₂ O wt%	CaO wt%	Na ₂ O wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	MgO wt%	TiO ₂ wt%	Total wt%
183LS1											
183LS1-1-1	L.O.D.	0.38	20.11	1.26	11.32	1.49	11.48	40.50	7.83	0.68	94.78
183LS1-1-2	L.O.D.	0.39	20.37	1.20	11.24	1.47	11.80	40.31	7.75	0.67	94.90
183LS1-1-3	L.O.D.	0.38	14.53	0.26	11.64	0.61	3.61	49.98	13.39	0.11	94.14
183LS1-1-4	L.O.D.	0.00	0.23	0.14	2.24	11.44	21.91	66.08	0.00	-0.01	102.00
183LS1-1-5	L.O.D.	0.08	4.10	0.20	2.96	0.25	1.78	85.10	2.41	0.04	96.77
183LS1-1-6	L.O.D.	0.38	17.12	0.56	11.48	1.00	7.19	45.92	11.02	0.29	94.64
183LS1-1-7	L.O.D.	-0.03	0.35	15.78	0.01	0.52	18.64	63.01	0.01	0.01	98.29
183LS1-1-8	L.O.D.	0.36	19.52	1.00	11.34	1.28	9.95	42.13	8.73	0.60	94.64
183LS1-2-7	L.O.D.	0.42	19.78	1.27	11.33	1.39	10.86	40.83	8.14	0.66	94.40
183LS1-2-8	L.O.D.	0.38	17.65	0.71	11.43	1.15	8.15	44.50	10.04	0.29	94.02
183LS1-2-9	L.O.D.	0.35	20.04	1.29	11.36	1.45	11.30	40.34	7.87	0.75	94.47
183LS1-2-10	L.O.D.	0.41	17.67	0.67	11.40	1.06	8.07	44.96	10.22	0.22	94.39
183LS1-2-11	0.22	0.36	15.16	0.34	11.64	0.61	4.02	49.51	12.98	0.08	94.81
183LS1-2-12	L.O.D.	0.39	20.30	1.23	11.38	1.39	11.30	40.65	8.11	0.75	95.21
183LS1-2-13	L.O.D.	0.36	20.47	1.27	11.27	1.38	11.48	40.15	7.75	0.65	94.54
183LS1-2-14	L.O.D.	0.38	13.94	0.16	11.80	0.43	2.28	51.98	14.39	0.03	95.06
183LS1-3-5	L.O.D.	0.30	19.75	8.70	0.17	0.09	15.82	36.99	11.24	1.37	94.16
183LS1-3-6	L.O.D.	0.41	19.76	1.16	11.23	1.36	10.83	41.04	8.22	0.49	94.71
183LS1-3-7	L.O.D.	0.39	13.94	0.23	11.85	0.47	2.71	51.42	14.10	0.06	94.82
183LS1-3-8	L.O.D.	0.43	18.55	0.97	11.35	1.29	9.82	42.64	9.23	0.33	94.32
183LS1-3-9	L.O.D.	0.40	18.29	0.88	11.29	1.26	8.99	43.62	9.66	0.44	94.50
183LS1-3-10	L.O.D.	0.37	16.52	0.54	11.47	1.15	7.21	46.01	11.12	0.27	94.35
183LS1-4-1	L.O.D.	0.37	18.04	0.74	11.47	1.16	8.44	44.15	10.02	0.34	94.43
183LS1-4-2	L.O.D.	0.38	13.34	0.15	11.96	0.39	2.45	51.60	14.39	0.06	94.36
183LS1-4-3	L.O.D.	0.39	20.92	1.41	11.24	1.43	12.18	39.79	7.29	0.56	95.37
183LS1-4-4	L.O.D.	0.38	18.84	1.22	11.21	1.21	9.83	42.05	9.06	0.43	93.95
183LS1-4-5	L.O.D.	0.37	17.38	0.76	11.51	1.07	8.02	44.49	10.54	0.65	94.48
183LS1-4-6	0.24	0.39	17.74	0.72	11.27	1.24	8.38	44.56	10.22	0.25	94.92
183LS1-4-7	L.O.D.	0.35	18.09	0.92	11.37	1.33	9.54	42.98	9.22	0.61	94.14
183LS1-4-8	L.O.D.	0.44	20.34	1.32	11.23	1.45	12.07	39.92	7.59	0.72	94.81
183LS1-4-9	L.O.D.	0.37	19.46	1.15	11.23	1.59	12.41	40.24	7.55	0.89	94.64
230LS1											
230LS1-1-1	L.O.D.	0.17	9.02	3.91	14.53	46.02	13.31	9.93	0.06	0.47	96.99
230LS1-1-2	L.O.D.	0.04	10.49	3.36	15.89	40.15	9.51	16.10	0.23	0.12	95.52
230LS1-1-3	L.O.D.	0.15	10.81	3.19	19.85	35.19	5.74	19.91	0.10	0.06	94.46
230LS1-1-3.5	L.O.D.	0.06	10.33	3.79	21.70	36.32	5.45	20.61	0.12	0.06	98.00
230LS1-1-4	L.O.D.	0.05	9.88	4.11	19.56	39.89	10.81	12.60	0.21	0.20	96.86
230LS1-2-3	L.O.D.	0.04	9.70	3.42	22.13	34.67	5.58	18.63	0.10	0.05	93.91
230LS1-2-4	L.O.D.	0.07	9.09	3.66	14.99	42.58	11.80	13.20	0.21	0.40	95.51
230LS1-2-6	L.O.D.	0.07	9.25	3.71	17.64	41.06	8.51	16.21	0.08	0.08	96.16
230LS1-2-7	L.O.D.	0.06	9.36	3.72	18.45	40.61	7.89	15.72	0.05	0.71	96.10
230LS1-3-4	L.O.D.	0.08	9.18	3.96	15.56	42.83	11.84	13.11	0.20	0.54	96.87
230LS1-3-5	L.O.D.	0.09	9.89	3.58	20.61	38.40	8.56	15.09	0.06	0.03	95.79
230LS1-3-6	L.O.D.	0.14	8.75	4.09	14.84	45.25	12.89	10.32	0.05	0.55	96.49
230LS1-3-7	L.O.D.	0.15	8.71	3.81	14.85	45.18	12.33	11.24	0.13	0.56	96.55
230LS1-4-3	L.O.D.	0.02	10.42	3.65	20.32	37.29	6.76	16.44	0.13	0.50	94.99
230LS1-4-4	L.O.D.	0.14	8.90	3.80	16.07	43.38	11.42	12.15	0.11	0.47	96.04
230LS1-5-15	L.O.D.	0.10	9.04	3.82	15.05	43.44	11.91	12.71	0.19	0.58	96.51
230LS1-5-16	L.O.D.	0.05	9.93	3.62	18.40	36.99	7.12	15.68	0.04	0.59	92.33
230LS1-5-17	L.O.D.	0.02	9.95	3.62	20.56	36.55	6.36	18.94	0.10	0.08	95.62
230LS1-5-18	L.O.D.	0.01	10.75	3.36	21.57	36.10	7.59	16.52	0.33	0.04	95.71
230LS1-6-1	L.O.D.	0.15	8.90	3.89	15.50	44.80	12.91	10.34	0.04	0.49	96.62
230LS1-6-2	L.O.D.	0.11	9.30	3.94	15.71	43.92	12.16	11.06	0.09	0.53	96.34
230LS1-6-3	L.O.D.	0.04	10.76	3.40	20.23	36.58	6.73	17.60	0.09	0.11	94.99
230LS1-6-4	L.O.D.	0.05	11.02	3.52	19.02	38.36	10.04	14.62	0.14	0.11	96.37
230LS1											
149LS1-2-5	L.O.D.	0.04	9.50	0.56	9.35	3.65	13.39	46.98	13.36	0.42	96.95
149LS1-2-6	L.O.D.	0.16	17.14	0.78	10.68	3.26	20.89	37.75	6.45	0.12	97.00
149LS1-2-1	L.O.D.	0.05	9.71	0.52	9.43	3.60	12.56	47.39	13.76	0.38	97.12
149LS1-2-2	L.O.D.	0.10	14.48	0.86	10.22	3.37	19.48	39.38	8.34	0.17	96.17
149LS1-1-3	L.O.D.	0.04	8.73	0.50	9.10	3.74	10.99	48.97	14.82	0.28	96.94
149LS1-1-5	L.O.D.	L.O.D.	9.69	0.66	9.23	3.96	14.60	45.81	12.68	0.43	96.87
149LS1-1-4	L.O.D.	0.04	9.37	0.54	9.26	3.92	13.11	46.73	13.37	0.40	96.49
149LS1-3-2	L.O.D.	0.04	4.88	0.00	15.86	5.69	8.85	54.86	9.93	0.06	99.88
149LS1-4-9	L.O.D.	0.01	9.28	0.54	9.43	3.62	11.42	48.28	14.28	0.32	96.92

Table A4 – IV: Clinopyroxene chemistry.

	MnO wt%	FeO wt%	K ₂ O wt%	CaO wt%	Na ₂ O wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	MgO wt%	TiO ₂ wt%	Cr ₂ O ₃ wt%	Total wt%
152LS1											
152LS1-5-5	0.02	6.58	0.02	14.92	6.21	8.47	55.36	9.24	0.12	0.03	100.95
152LS1-5-7	0.02	6.56	0.00	14.98	6.00	8.46	55.15	9.20	0.13	0.04	100.55
152LS1-5-6	0.03	6.76	0.01	14.96	6.09	8.43	55.14	9.14	0.08	0.04	100.68
152LS1-5-6	0.03	6.66	0.01	14.99	6.06	8.55	55.56	9.13	0.06	0.04	101.07
152LS1-5-7	0.02	6.58	L.O.D.	14.97	6.01	8.62	55.19	9.21	0.09	0.03	100.71
152LS1-5-18	0.03	6.51	0.00	14.97	6.10	8.40	55.21	9.15	0.11	0.03	100.50
152LS1-5-8	0.02	6.00	0.01	14.89	6.14	8.58	55.34	9.29	0.04	0.03	100.34
152LS1-5-10	0.02	5.72	0.03	15.27	6.09	9.06	56.11	9.82	0.11	0.05	102.29
152LS1-5-9	0.02	6.60	0.01	14.96	5.97	8.52	55.39	9.16	0.16	0.02	100.83
152LS1-5-8	0.01	6.30	0.01	15.00	6.25	8.59	55.33	9.34	0.11	0.01	100.96
152LS1-5-9	0.06	6.78	0.00	14.88	5.91	8.36	55.38	9.08	0.12	0.04	100.62
152LS1-5-10	L.O.D.	6.04	0.00	15.12	6.20	8.57	55.53	9.36	0.07	0.02	100.91
152LS1-2-5	0.03	6.76	0.01	14.83	6.18	8.42	55.14	9.05	0.13	0.04	100.59
152LS1-2-5	L.O.D.	6.71	0.01	14.97	6.07	8.48	54.97	9.16	0.13	0.03	100.52
152LS1-6-4	0.02	6.48	0.01	14.97	6.29	8.56	55.10	9.11	0.09	0.05	100.68
152LS1-7-3	0.04	6.64	0.00	15.00	6.05	8.50	55.10	9.16	0.08	0.07	100.64
152LS1-9-7	0.01	6.74	0.00	15.02	6.11	8.40	55.25	9.10	0.11	0.04	100.77
152LS1-9-6	0.02	10.31	0.67	9.12	3.60	12.99	46.71	13.26	0.35	0.00	97.03
152LS1-10-4	0.02	6.57	0.01	14.91	6.14	8.52	54.62	9.06	0.10	0.03	99.99
152LS1-10-3	0.00	6.66	0.00	14.85	5.91	8.38	54.85	9.00	0.11	0.02	99.78
152LS1-10-2	0.00	6.56	0.01	15.05	6.13	8.39	55.40	9.14	0.11	0.02	100.80
152LS1-10-1	0.03	6.48	0.01	14.92	6.12	8.45	55.04	9.11	0.09	0.02	100.28
152LS1-3-8	0.05	5.76	0.00	15.03	5.47	8.73	55.17	9.23	0.08	0.01	99.53
152LS1-3-9	0.01	6.41	0.02	15.01	5.24	8.27	54.92	9.24	0.07	0.01	99.19
152LS1-3-10	0.03	4.29	0.02	23.24	0.01	31.28	39.93	0.11	0.12	0.01	99.03
152LS1-3-11	0.07	6.13	0.10	9.45	3.33	13.93	48.31	15.48	0.31	0.00	97.11
152LS1-3-12	0.06	4.16	0.01	23.52	0.02	31.20	39.69	0.14	0.12	0.02	98.89
149LS1											
149LS1-1-7	0.02	4.48	0.01	14.94	6.13	9.97	55.52	9.29	0.10	0.03	100.48
149LS1-1-6	0.01	1.88	9.14	0.03	0.58	31.15	53.30	3.50	0.61	0.05	100.26
149LS1-5-2	0.04	4.13	0.00	15.42	5.97	9.60	55.78	9.83	0.04	0.03	100.84
149LS1-5-1	0.00	4.38	0.00	15.13	6.11	9.67	55.74	9.61	0.09	0.01	100.74
149LS1-3-7	0.04	4.38	L.O.D.	15.11	6.33	9.76	55.59	9.39	0.12	0.04	100.75
149LS1-3-8	0.00	4.52	0.00	15.12	6.22	9.90	55.91	9.43	0.09	0.03	101.22
149LS1-3-5	0.05	4.54	0.00	15.02	6.34	9.85	55.81	9.43	0.11	0.02	101.17
149LS1-4-3	0.02	4.56	0.00	15.32	6.21	9.84	56.04	9.65	0.06	0.03	101.73
149LS1-4-9	0.04	4.50	0.01	15.10	6.23	9.83	55.94	9.46	0.09	0.03	101.24
230LS1											
230LS1-1-16	L.O.D.	0.01	14.12	5.96	10.96	55.41	8.51	4.66	0.04	0.17	99.83
230LS1-2-1	L.O.D.	0.00	14.00	6.39	11.20	55.60	8.66	4.39	0.04	0.16	100.43
230LS1-2-2	L.O.D.	0.00	14.39	6.16	10.47	55.65	9.14	4.48	0.03	0.17	100.49
230LS1-3-11	L.O.D.	0.00	13.92	6.33	11.12	55.39	8.48	4.40	0.03	0.14	99.82
230LS1-3-12	L.O.D.	0.01	13.98	6.28	11.10	55.38	8.71	4.60	0.03	0.16	100.23
230LS1-4-7	L.O.D.	L.O.D.	13.98	6.34	11.14	55.24	8.58	4.26	0.01	0.14	99.69
230LS1-4-8	L.O.D.	0.00	14.36	5.94	10.55	55.44	8.93	4.82	0.06	0.15	100.25
230LS1-4-9	L.O.D.	L.O.D.	15.40	5.48	9.35	55.83	9.95	4.32	0.00	0.10	100.44
230LS1-4-10	L.O.D.	0.00	14.48	6.09	10.55	55.46	9.05	4.48	0.04	0.11	100.25
230LS1-5-3	L.O.D.	0.00	13.94	6.34	11.16	55.40	8.70	4.49	0.04	0.12	100.19
230LS1-5-4	L.O.D.	0.00	14.24	5.94	10.69	55.50	8.77	4.42	0.06	0.15	99.75
230LS1-5-5	L.O.D.	0.00	14.15	6.18	10.69	55.56	9.08	4.04	0.02	0.08	99.80
230LS1-5-6	L.O.D.	0.00	13.96	6.36	11.04	55.70	8.73	4.35	0.01	0.15	100.30
230LS1-5-7	L.O.D.	0.00	13.88	6.22	11.53	55.02	8.36	4.55	0.00	0.17	99.73
230LS1-5-8	L.O.D.	0.01	13.88	6.27	11.32	55.56	8.43	4.69	0.04	0.16	100.33
230LS1-6-15	L.O.D.	0.00	14.25	6.16	10.66	55.13	8.78	4.46	0.01	0.13	99.58
93LS1a											
93LS1a-1-13	L.O.D.	0.01	14.08	6.09	7.33	55.17	8.05	9.11	0.01	0.09	99.92
93LS1a-1-14	L.O.D.	0.00	14.59	5.91	7.12	55.79	8.88	8.83	0.07	0.10	101.28
93LS1a-2-1	L.O.D.	0.00	13.94	5.87	6.88	54.67	8.06	9.30	0.01	0.08	98.81
93LS1a-3-8	L.O.D.	0.00	13.98	5.88	6.58	54.92	8.41	8.92	0.02	0.05	98.77
93LS1a-4-9	L.O.D.	0.00	14.18	5.88	6.48	55.14	8.56	8.89	0.04	0.08	99.24

Table A4 – V: White mica chemistry.

	F wt%	MnO wt%	FeO wt%	K ₂ O wt%	CaO wt%	Na ₂ O wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	MgO wt%	TiO ₂ wt%	Total wt%
152LS1											
152LS1-5-3-Wm	L.O.D.	L.O.D.	1.91	9.43	0.00	0.42	29.86	55.02	4.09	0.58	101.20
152LS1-5-4-Wm	L.O.D.	0.01	2.04	9.18	0.00	0.38	28.83	54.88	4.29	0.75	100.27
152LS1-4-1-Wm	L.O.D.	0.03	2.02	9.21	L.O.D.	0.32	29.59	55.40	4.30	0.65	101.44
152LS1-4-2-Wm	L.O.D.	L.O.D.	2.01	9.11	0.00	0.34	28.75	54.66	4.36	0.85	99.94
152LS1-4-3-Wm	L.O.D.	L.O.D.	2.15	9.06	0.00	0.26	29.10	54.96	4.30	0.64	100.34
152LS1-4-4-Wm	L.O.D.	0.01	1.97	8.95	0.01	0.28	30.49	54.38	3.69	0.61	100.29
152LS1-4-5-Wm	L.O.D.	0.01	2.07	9.35	L.O.D.	0.30	28.63	54.46	4.43	0.76	99.92
152LS1-3-3-Wm	L.O.D.	0.01	1.93	9.23	0.01	0.35	28.69	55.20	4.39	0.84	100.57
152LS1-3-2-Wm	L.O.D.	0.02	2.25	9.49	L.O.D.	0.25	28.67	54.34	4.07	0.81	99.79
152LS1-3-1-Wm	L.O.D.	0.01	2.08	9.43	L.O.D.	0.34	29.80	54.86	4.16	0.61	101.17
152LS1-2-6-Wm	L.O.D.	0.00	2.38	9.15	L.O.D.	0.21	28.43	54.83	4.43	0.83	100.12
152LS1-2-7-Wm	L.O.D.	0.00	2.17	9.03	L.O.D.	0.29	28.84	55.03	4.31	0.81	100.37
152LS1-6-3-Wm	L.O.D.	L.O.D.	1.98	8.82	0.04	0.32	28.71	55.06	4.45	0.78	100.05
152LS1-7-8-Wm	L.O.D.	0.00	1.92	9.52	0.01	0.28	28.67	55.01	4.48	0.69	100.47
152LS1-9-8-Wm	L.O.D.	0.00	2.01	9.53	0.00	0.23	29.54	55.06	4.14	0.55	100.93
152LS1-9-9-Wm	L.O.D.	L.O.D.	2.20	9.58	0.02	0.23	28.03	55.45	4.82	0.70	100.91
152LS1-10-9-Wm	L.O.D.	0.00	2.22	9.44	0.01	0.25	28.85	55.06	4.48	0.54	100.76
152LS1-10-10-Wm	L.O.D.	0.00	1.80	9.33	0.01	0.38	28.99	54.46	4.25	0.79	99.93
152LS1-10-11-Wm	L.O.D.	0.01	1.96	9.05	0.00	0.34	28.99	55.18	4.35	0.81	100.59
152LS1-10-12-Wm	L.O.D.	0.02	1.96	9.40	L.O.D.	0.35	28.69	55.05	4.44	0.81	100.63
152LS1-10-13-Wm	L.O.D.	0.01	1.89	9.12	0.03	0.43	28.89	54.61	4.38	0.81	100.07
93LS1a											
93LS1a-2-6	L.O.D.	10.61	0.02	0.19	24.84	54.64	4.43	3.28	0.01	0.81	98.70
93LS1a-3-5	L.O.D.	10.80	0.01	0.26	25.61	53.89	4.18	3.30	0.01	0.87	98.81
93LS1a-3-6	L.O.D.	10.13	0.01	0.14	24.77	54.51	4.64	3.66	0.00	0.92	98.65
93LS1a-3-7	L.O.D.	9.82	0.02	0.43	28.86	51.97	3.13	3.77	L.O.D.	0.54	98.47
93LS1a-4-12	L.O.D.	10.07	0.02	0.31	25.96	54.85	4.18	3.29	L.O.D.	1.06	99.59
93LS1a-4-13	L.O.D.	9.93	0.02	0.41	28.01	52.63	3.49	3.49	0.02	0.63	98.50
149LS1											
149LS1-5-4-Wm	L.O.D.	0.02	1.73	9.22	0.01	0.38	29.31	54.92	4.26	0.74	100.51
149LS1-5-3-Wm	L.O.D.	0.01	1.74	9.14	0.00	0.35	28.92	54.96	4.53	0.57	100.12
149LS1-3-5-Wm	L.O.D.	0.02	1.86	8.94	L.O.D.	0.40	28.74	55.53	4.35	0.62	100.35
149LS1-3-4-Wm	L.O.D.	0.01	1.77	9.01	L.O.D.	0.34	29.09	54.92	4.39	0.68	100.12
149LS1-4-2-Wm	L.O.D.	0.00	1.85	8.96	L.O.D.	0.45	29.20	54.74	4.17	0.70	99.96

Table A4 – VI: Garnet chemistry.

	FeO wt%	MnO wt%	CaO wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	MgO wt%	Cr ₂ O ₃ wt%	TiO ₂ wt%	Total wt%
93LS1a									
93LS1-a T1 Line 001	28.60	0.76	6.45	21.70	37.78	4.50	L.O.D.	0.07	99.85
93LS1-a T1 Line 002	29.20	0.76	5.87	21.81	38.19	4.65	L.O.D.	0.03	100.52
93LS1-a T1 Line 003	29.08	0.79	5.46	21.57	37.59	4.66	L.O.D.	0.06	99.21
93LS1-a T1 Line 004	29.63	0.75	5.46	21.71	37.63	4.72	L.O.D.	0.06	99.97
93LS1-a T1 Line 005	29.07	0.82	5.41	21.64	37.48	4.82	0.02	0.04	99.29
93LS1-a T1 Line 006	29.67	0.78	5.25	21.69	37.65	4.84	0.01	0.03	99.92
93LS1-a T1 Line 007	30.10	0.80	5.02	21.87	38.03	4.94	0.01	0.01	100.79
93LS1-a T1 Line 008	29.99	0.78	4.98	21.85	37.76	4.75	L.O.D.	0.04	100.14
93LS1-a T1 Line 009	30.07	0.76	4.99	21.82	37.76	4.59	L.O.D.	0.05	100.04
93LS1-a T1 Line 010	30.09	0.72	4.98	21.72	37.69	4.57	0.00	0.04	99.82
93LS1-a T1 Line 011	30.06	0.72	5.04	21.67	37.66	4.49	L.O.D.	0.06	99.68
93LS1-a T1 Line 012	29.96	0.75	5.19	22.00	37.90	4.62	0.02	0.06	100.50
93LS1-a T1 Line 013	30.80	0.72	5.26	21.80	37.77	4.20	0.02	0.07	100.63
93LS1-a T1 Line 014	31.27	0.70	5.12	21.63	37.77	3.88	L.O.D.	0.06	100.42
93LS1-a T1 Line 015	31.57	0.73	5.17	21.55	37.52	3.76	L.O.D.	0.06	100.36
93LS1-a T1 Line 016	31.82	0.90	5.23	21.50	37.24	3.17	0.01	0.05	99.93
93LS1-a T1 Line 017	28.97	0.99	8.66	21.77	37.53	2.47	0.01	0.03	100.42
93LS1-a T1 Line 018	27.84	0.76	9.12	21.47	37.58	2.65	0.01	0.06	99.50
93LS1-a T1 Line 019	27.45	0.88	10.38	21.52	37.81	2.22	0.01	0.10	100.37
93LS1-a T1 Line 020	15.99	0.35	11.72	11.43	45.67	5.45	0.02	0.11	90.73
93LS1-a T1 Line 021	30.64	0.82	7.15	21.57	37.58	2.83	0.02	0.05	100.67
93LS1-a T1 Line 022	30.00	0.76	7.45	21.79	37.97	3.20	L.O.D.	0.04	101.21
93LS1-a T1 Line 023	28.84	0.64	7.40	21.57	37.69	3.88	0.01	0.02	100.07
93LS1-a T1 Line 024	30.18	0.87	7.33	21.32	37.47	2.87	0.04	0.07	100.15
93LS1-a T1 Line 025	31.05	0.83	6.74	21.45	37.71	2.89	L.O.D.	0.05	100.71
93LS1-a T1 Line 026	31.46	1.00	6.23	21.57	37.69	2.81	L.O.D.	0.05	100.77
93LS1-a T1 Line 027	32.13	0.81	4.90	21.53	37.18	3.51	L.O.D.	0.02	100.07
93LS1-a T1 Line 028	30.18	0.74	6.39	21.70	37.58	3.51	0.01	0.04	100.15
93LS1-a T1 Line 029	31.66	0.84	5.36	21.74	37.49	3.40	L.O.D.	0.02	100.50
93LS1-a T1 Line 030	32.32	0.98	4.99	21.67	37.49	3.15	L.O.D.	0.05	100.64
93LS1-a T1 Line 031	28.03	0.98	9.90	21.65	37.64	2.15	L.O.D.	0.05	100.40
93LS1-a T1 Line 032	28.45	0.98	9.56	21.85	37.80	2.26	L.O.D.	0.06	100.95
93LS1-a T1 Line 033	28.72	0.71	8.53	21.75	37.69	3.12	0.00	0.05	100.57
93LS1-a T1 Line 034	28.15	0.66	9.28	21.05	37.70	3.11	0.01	0.26	100.22
93LS1-a T1 Line 035	27.42	0.54	9.81	21.02	37.63	3.55	0.01	0.16	100.14
93LS1-a T1 Line 036	27.65	0.56	9.52	21.05	37.79	3.36	0.01	0.13	100.07
93LS1-a T1 Line 037	28.65	0.68	8.91	21.33	37.83	3.19	0.02	0.08	100.68
93LS1-a T1 Line 038	28.74	0.62	8.93	21.18	37.81	3.34	0.00	0.14	100.76
93LS1-a T1 Line 039	27.68	0.50	8.84	21.67	38.09	3.94	0.01	0.08	100.81
93LS1-a T1 Line 040	28.05	0.48	8.33	21.62	38.01	3.96	0.01	0.08	100.54
93LS1-a T1 Line 041	28.91	0.59	7.88	21.73	37.87	3.68	L.O.D.	0.07	100.71
93LS1-a T1 Line 042	28.04	0.46	7.74	22.10	37.91	4.20	L.O.D.	0.05	100.48
93LS1-a T1 Line 043	29.46	0.69	7.52	21.82	37.71	3.38	L.O.D.	0.05	100.62
93LS1-a T1 Line 044	30.12	0.79	6.37	21.61	37.90	3.54	L.O.D.	0.03	100.36
93LS1-a T1 Line 045	29.41	0.67	6.69	21.97	38.15	4.11	0.00	0.04	101.03
93LS1-a T1 Line 046	28.59	0.66	6.99	21.74	37.90	4.41	0.00	0.08	100.37
93LS1-a T1 Line 047	28.55	0.67	7.07	21.76	37.98	4.33	0.02	0.06	100.44
93LS1-a T1 Line 048	28.32	0.66	7.23	21.70	37.92	4.31	0.01	0.08	100.23
93LS1-a T1 Line 049	28.01	0.65	7.19	21.94	38.12	4.33	0.02	0.10	100.36
93LS1-a T1 Line 050	29.65	0.72	7.03	22.56	38.72	3.75	0.01	0.06	102.49

Table A4 – VI: (Continued)

	FeO wt%	MnO wt%	CaO wt%	Al ₂ O ₃ wt%	SiO ₂ wt%	MgO wt%	Cr ₂ O ₃ wt%	TiO ₂ wt%	Total wt%
93LS1-a T2 Line 001	29.38	0.78	7.46	21.33	37.22	3.12	0.01	0.06	99.36
93LS1-a T2 Line 002	29.86	0.77	7.19	21.45	37.37	3.35	L.O.D.	0.04	100.02
93LS1-a T2 Line 003	29.10	0.64	7.18	21.73	37.79	4.00	0.00	0.05	100.49
93LS1-a T2 Line 004	28.52	0.62	7.36	21.77	37.61	3.99	0.00	0.07	99.94
93LS1-a T2 Line 005	28.86	0.65	7.26	21.69	37.71	3.73	0.01	0.10	100.01
93LS1-a T2 Line 006	28.56	0.60	7.78	21.64	37.86	3.70	0.00	0.17	100.31
93LS1-a T2 Line 007	28.47	0.76	9.01	21.23	37.47	2.83	0.02	0.62	100.40
93LS1-a T2 Line 008	28.67	0.74	8.44	20.93	37.19	2.74	0.01	1.52	100.25
93LS1-a T2 Line 009	36.78	0.20	1.01	2.06	3.17	0.39	0.00	57.85	101.46
93LS1-a T2 Line 010	27.77	0.80	10.01	21.86	37.69	2.41	L.O.D.	0.17	100.70
93LS1-a T2 Line 011	29.69	0.69	7.55	21.90	37.78	3.19	L.O.D.	0.06	100.89
93LS1-a T2 Line 012	31.74	1.05	5.69	21.45	37.29	2.87	L.O.D.	0.05	100.11
93LS1-a T2 Line 013	32.19	0.88	5.17	21.79	37.59	3.27	L.O.D.	0.02	100.89
93LS1-a T2 Line 014	29.80	0.80	7.55	21.74	37.70	2.97	L.O.D.	0.05	100.60
93LS1-a T2 Line 015	28.77	0.78	9.36	21.00	37.55	2.68	L.O.D.	0.13	100.28
93LS1-a T2 Line 016	28.01	0.68	10.02	20.93	37.72	2.86	0.01	0.19	100.41
93LS1-a T2 Line 017	29.04	0.77	8.60	21.04	37.53	2.93	0.00	0.11	100.02
93LS1-a T2 Line 018	26.75	0.68	6.59	18.50	45.52	2.77	0.01	0.08	100.90
93LS1-a T2 Line 019	28.91	0.77	8.74	21.03	37.61	2.89	0.00	0.13	100.09
93LS1-a T2 Line 020	29.12	0.80	9.03	21.02	37.80	2.85	0.00	0.11	100.73
93LS1-a T2 Line 021	27.93	0.64	9.50	21.23	37.70	3.10	L.O.D.	0.10	100.20
93LS1-a T2 Line 022	28.63	0.78	9.43	21.16	37.47	2.61	0.01	0.13	100.21
93LS1-a T2 Line 023	28.17	1.01	9.61	21.89	37.47	2.27	0.00	0.03	100.47
93LS1-a T2 Line 024	32.15	0.90	4.94	21.68	37.39	3.33	L.O.D.	0.03	100.41
93LS1-a T2 Line 025	32.18	0.94	5.29	21.55	37.37	3.09	L.O.D.	0.02	100.43
93LS1-a T2 Line 026	28.57	0.97	9.07	21.94	37.74	2.33	0.01	0.03	100.67
93LS1-a T2 Line 027	31.92	0.85	5.33	21.83	37.50	3.28	0.01	0.03	100.75
93LS1-a T2 Line 028	28.05	1.01	9.79	21.77	37.57	2.13	0.01	0.04	100.37
93LS1-a T2 Line 029	27.94	0.62	9.40	21.34	37.95	3.07	0.00	0.13	100.45
93LS1-a T2 Line 030	27.18	0.67	9.62	21.85	38.02	3.38	L.O.D.	0.12	100.82
93LS1-a T2 Line 031	26.90	0.63	10.14	21.43	37.49	3.13	0.01	0.14	99.89
93LS1-a T2 Line 032	26.65	0.62	10.55	21.43	38.01	3.11	0.00	0.15	100.53
93LS1-a T2 Line 033	25.96	0.59	10.66	21.32	38.04	3.32	L.O.D.	0.20	100.08
93LS1-a T2 Line 034	26.38	0.61	10.55	21.54	37.79	3.39	0.00	0.16	100.42
93LS1-a T2 Line 035	26.26	0.60	10.63	21.34	37.36	3.27	0.00	0.17	99.63
93LS1-a T2 Line 036	26.48	0.58	10.69	21.08	37.79	3.30	0.00	0.20	100.13
93LS1-a T2 Line 037	26.81	0.58	10.52	21.28	38.20	3.33	L.O.D.	0.18	100.88
93LS1-a T2 Line 038	26.81	0.55	10.39	21.08	37.79	3.43	0.01	0.19	100.26
93LS1-a T2 Line 039	26.96	0.57	10.29	20.94	37.76	3.48	L.O.D.	0.19	100.17
93LS1-a T2 Line 040	27.25	0.57	10.16	21.14	37.78	3.44	0.02	0.15	100.51
93LS1-a T2 Line 041	27.66	0.65	9.50	21.29	37.61	3.23	0.00	0.11	100.05
93LS1-a T2 Line 042	28.70	0.69	8.69	21.72	37.65	3.03	L.O.D.	0.06	100.53
93LS1-a T2 Line 043	28.84	0.77	8.35	21.96	37.70	2.96	0.01	0.02	100.60
93LS1-a T2 Line 044	30.58	0.79	6.34	21.94	37.78	3.33	L.O.D.	0.03	100.79
93LS1-a T2 Line 045	30.19	0.77	6.81	21.75	37.88	3.28	L.O.D.	0.03	100.71
line T1 and T2 = points along a traverse on garnet sample from 93LS1a									

Table A4 – VII: Rutile chemistry.

93LS1c										
	FeO	Nb ₂ O ₅	TiO ₂	Total			FeO	Nb ₂ O ₅	TiO ₂	Total
93LS1- R0G1	0.33	0.06	99.38	99.77		93LS1- R5G9	0.19	0.05	99.03	99.28
93LS1- R1G1	0.24	0.06	99.26	99.56		93LS1- R5G10 core	0.28	0.05	99.07	99.40
93LS1- R1G2	0.31	0.04	99.26	99.61		93LS1- R5G10 rim	0.27	0.05	100.00	100.32
93LS1- R1G3	0.23	0.06	99.58	99.88		93LS1- R6G1 core	0.26	0.05	99.59	99.90
93LS1- R1G4	0.27	0.06	99.50	99.83		93LS1- R6G1 rim	0.31	0.07	99.04	99.42
93LS1- R1G5	0.29	0.04	99.11	99.44		93LS1- R6G2	0.27	0.03	98.96	99.25
93LS1- R1G6	0.31	0.05	99.29	99.65		93LS1- R6G3	0.30	0.06	99.32	99.68
93LS1- R1G7	0.32	0.06	99.41	99.79		93LS1- R6G5	0.35	0.05	99.72	100.13
93LS1- R1G8	0.27	0.06	99.18	99.51		93LS1- R6G6 rim	0.33	0.05	99.17	99.56
93LS1- R1G9	0.28	0.05	100.17	100.50		93LS1- R6G6 core	0.34	0.05	99.68	100.07
93LS1- R1G10	0.30	0.05	99.39	99.74		93LS1- R6G8	0.32	0.04	99.81	100.18
93LS1- R2G1	0.28	0.04	99.80	100.13		93LS1- R6G9	0.30	0.05	99.61	99.97
93LS1- R2G2	0.32	0.06	99.36	99.73		93LS1- R7G1 rim	0.48	0.09	99.70	100.26
93LS1- R2G3	0.31	0.04	99.32	99.68		93LS1- R7G1 core	0.55	0.05	99.89	100.50
93LS1- R2G4	0.30	0.06	99.86	100.22		93LS1- R7G2	0.22	0.07	99.66	99.96
93LS1- R2G5	0.40	0.08	99.35	99.83		93LS1- R7G3 rim	0.30	0.04	99.66	100.00
93LS1- R2G6	0.32	0.05	99.13	99.50		93LS1- R7G3 rim	0.27	0.05	99.02	99.33
93LS1- R2G7	0.28	0.05	99.90	100.23		93LS1- R7G4	0.29	0.05	99.50	99.83
93LS1- R2G8	0.28	0.05	99.59	99.92		93LS1- R7G5	0.31	0.05	99.67	100.03
93LS1- R2G9	0.33	0.06	99.54	99.93		93LS1- R7G6	0.27	0.06	99.87	100.20
93LS1- R2G10	0.22	0.05	99.46	99.72		93LS1- R7G7	0.25	0.08	99.07	99.39
93LS1- R3G1	0.29	0.05	99.09	99.43		93LS1- R7G8	0.27	0.04	99.72	100.03
93LS1- R3G2	0.24	0.06	99.67	99.96		93LS1- R7G9	0.24	0.05	99.41	99.69
93LS1- R3G3	0.55	0.05	99.60	100.19		93LS1- R7G10	0.24	0.05	99.72	100.00
93LS1- R3G4	0.26	0.05	99.90	100.20		93LS1- R8G1 core	0.57	0.05	99.04	99.65
93LS1- R3G5	0.29	0.06	99.44	99.79		93LS1- R8G1 rim	0.45	0.05	99.47	99.96
93LS1- R3G6	0.31	0.05	99.55	99.91		93LS1- R8G2	0.28	0.04	99.55	99.87
93LS1- R3G7	0.26	0.05	99.36	99.68		93LS1- R8G3	0.35	0.06	99.33	99.74
93LS1- R3G8	0.28	0.05	100.02	100.36		93LS1- R8G4	0.24	0.06	99.44	99.74
93LS1- R3G10	0.29	0.05	99.59	99.93		93LS1- R8G6	0.39	0.05	99.50	99.94
93LS1- R4G1	0.28	0.05	99.35	99.68		93LS1- R8G7	0.24	0.05	99.47	99.75
93LS1- R4G2	0.28	0.06	99.65	99.99		93LS1- R8G8 core	0.32	0.05	99.56	99.93
93LS1- R4G3 core	0.29	0.05	99.49	99.82		93LS1- R8G8 rim	0.29	0.05	99.38	99.72
93LS1- R4G3 rim	0.29	0.05	99.34	99.69		93LS1- R8G9	0.25	0.05	99.25	99.55
93LS1- R4G4	0.28	0.03	99.45	99.76		93LS1- R8G10	0.34	0.05	99.38	99.77
93LS1- R4G5	0.27	0.05	99.67	99.99		93LS1- R9G1	0.29	0.05	99.44	99.77
93LS1- R4G6	0.28	0.05	99.52	99.86		93LS1- R9G2	0.30	0.04	99.52	99.86
93LS1- R4G9 rim	0.31	0.07	99.38	99.76		93LS1- R9G3	0.25	0.05	99.56	99.87
93LS1- R4G9 core	0.33	0.04	99.46	99.83		93LS1- R9G5	0.22	0.05	99.37	99.64
93LS1- R4G10	0.52	0.07	99.15	99.75		93LS1- R9G6	0.29	0.06	99.96	100.31
93LS1- R5G1 core	0.30	0.06	99.76	100.12		93LS1- R9G8	0.29	0.05	99.25	99.59
93LS1- R5G3	0.29	0.04	99.43	99.77		93LS1- R10G2	0.26	0.05	99.69	100.01
93LS1- R5G4	0.27	0.05	99.11	99.42		93LS1- R10G3	0.24	0.00	99.65	99.90
93LS1- R5G5	0.26	0.05	99.64	99.94		93LS1- R10G7	0.30	0.05	99.23	99.57
93LS1- R5G6	0.31	0.05	99.69	100.06		93LS1- R10G9	0.27	0.06	100.17	100.51
93LS1- R5G7	0.25	0.05	100.06	100.37						

Table A4 – VII: (Continued)

152LS1										
EPMA wt%	FeO	Nb ₂ O ₅	TiO ₂	Total			FeO	Nb ₂ O ₅	TiO ₂	Total
152LS1- R1G1	0.21	0.05	99.77	100.03		152LS1- R7G4	0.21	0.04	99.39	99.64
152LS1- R1G2	0.25	0.04	99.62	99.91		152LS1- R7G5	0.27	0.04	99.92	100.22
152LS1- R1G3	1.11	0.05	95.22	96.38		152LS1- R7G6	0.25	0.05	99.39	99.69
152LS1- R1G4	0.35	0.05	99.12	99.52		152LS1- R7G7	0.19	0.04	100.29	100.52
152LS1- R1G5	0.24	0.06	99.20	99.50		152LS1- R7G8	0.26	0.05	99.88	100.18
152LS1- R1G6	0.25	0.04	99.41	99.70		152LS1- R7G9	0.20	0.05	100.26	100.52
152LS1- R1G7	0.21	0.04	99.48	99.73		152LS1- R7G10	0.24	0.05	99.66	99.94
152LS1- R1G8	0.13	0.06	99.86	100.06		152LS1- R8G1	0.24	0.06	99.67	99.98
152LS1- R1G9	0.16	0.04	99.56	99.76		152LS1- R8G2	0.22	0.04	99.78	100.03
152LS1- R1G10	0.24	0.06	99.85	100.16		152LS1- R8G4	0.21	0.05	99.91	100.17
152LS1- R2G2	0.23	0.05	99.71	100.00		152LS1- R8G5	0.22	0.04	100.20	100.46
152LS1- R2G3	0.22	0.03	99.57	99.83		152LS1- R8G6	0.19	0.05	99.98	100.22
152LS1- R2G4	0.21	0.04	99.61	99.86		152LS1- R8G8	0.25	0.08	99.92	100.25
152LS1- R2G5	0.17	0.05	99.91	100.13		152LS1- R8G9	0.20	0.05	99.97	100.23
152LS1- R2G6	0.21	0.05	99.78	100.04		152LS1- R8G10	0.22	0.04	99.74	100.00
152LS1- R2G9	0.20	0.06	99.68	99.93		152LS1- R9G3	0.22	0.04	98.91	99.17
152LS1- R3G1	0.21	0.04	99.19	99.44		152LS1- R9G4	0.24	0.05	99.69	99.98
152LS1- R3G2	0.24	0.04	99.81	100.09		152LS1- R9G5	0.27	0.05	99.92	100.23
152LS1- R3G3	0.27	0.04	99.55	99.86		152LS1- R9G6	0.24	0.05	100.11	100.39
152LS1- R3G4	0.26	0.05	100.23	100.54		152LS1- R9G8	0.15	0.03	99.90	100.08
152LS1- R3G5	0.15	0.05	100.07	100.27		152LS1- R9G9	0.16	0.05	99.89	100.10
152LS1- R3G6	0.16	0.04	99.22	99.41		152LS1- R9G10	0.22	0.05	99.43	99.70
152LS1- R3G7	0.28	0.04	99.88	100.20		152LS1- R10G3	0.20	0.06	100.09	100.34
152LS1- R3G9	0.15	0.05	99.80	100.00		152LS1- R10G4	0.27	0.05	99.37	99.68
152LS1- R4G2	0.20	0.04	99.60	99.83		152LS1- R10G6	0.24	0.09	99.27	99.60
152LS1- R4G3	0.27	0.06	99.89	100.22		152LS1- R10G9	0.19	0.06	99.38	99.63
152LS1- R4G4	0.15	0.05	99.58	99.78		152LS1- R10G10	0.17	0.04	99.65	99.86
152LS1- R4G7	0.21	0.05	99.74	100.00		152LS1 1 3	0.24	0.05	99.03	99.32
152LS1- R4G8	0.29	0.03	99.18	99.50		152LS1 1 2	0.28	0.04	97.36	97.68
152LS1- R4G9	0.25	0.03	99.56	99.83		152LS1 1 1	0.31	0.06	98.61	98.98
152LS1- R4G10	0.25	0.06	99.32	99.63		152LS1 2 1	0.33	0.05	98.81	99.20
152LS1- R5G2	0.23	0.05	99.50	99.78		152LS1 2 2	0.51	0.08	97.85	98.43
152LS1- R5G5	0.24	0.06	100.04	100.34		152LS1 2 3	0.30	0.06	98.75	99.11
152LS1- R5G6	0.25	0.05	99.32	99.62		152LS1 2 4	0.26	0.05	98.85	99.16
152LS1- R5G7	0.21	0.07	99.32	99.59		152LS1 2 5	0.43	0.00	6.92	7.35
152LS1- R5G8	0.16	0.07	99.42	99.65		152LS1 2 6	0.25	0.06	98.57	98.88
152LS1- R5G9	0.17	0.04	99.90	100.11		152LS1 2 7	0.26	0.04	98.82	99.12
152LS1- R5G10	0.24	0.02	99.45	99.71		152LS1 3 1	0.27	0.05	98.63	98.94
152LS1- R6G3	0.12	0.03	99.71	99.85		152LS1 3 2	0.29	0.05	98.79	99.12
152LS1- R6G4	0.28	0.04	99.47	99.79		152LS1 3 3	0.28	0.05	99.13	99.47
152LS1- R6G5	0.21	0.03	99.80	100.04		152LS1 3 5	0.30	0.03	98.22	98.56
152LS1- R6G9	0.18	0.05	100.18	100.41		152LS1 3 7	0.19	0.04	97.72	97.95
152LS1- R6G10	0.29	0.05	99.58	99.92		152LS1 4 1	0.17	0.04	99.48	99.69
152LS1- R7G1	0.96	0.04	99.19	100.19		152LS1 4 4	0.30	0.04	99.18	99.52
152LS1- R7G2	0.28	0.06	99.48	99.81		152LS1 4 5	0.57	0.08	96.60	97.25
152LS1 7 2	0.76	0.04	84.32	85.12		152LS1 5 1	0.22	0.05	99.14	99.40
152LS1 7 4	0.27	0.06	99.38	99.71		152LS1 5 2	0.25	0.03	98.79	99.07
152LS1 7 3	0.33	0.03	98.54	98.91		152LS1 5 3	0.40	0.04	99.39	99.84
152LS1 7 b1	0.38	0.05	99.08	99.52		152LS1 7 1	0.43	0.03	93.00	93.46

Table A4 – VII: (Continued)

230LS1											
EPMA wt%	FeO	ZrO2	Ta ₂ O ₅	CaO	Nb ₂ O ₅	Al ₂ O ₃	SiO ₂	HfO ₂	Cr ₂ O ₃	TiO ₂	Total
230LS1 G1 P1	0.30	0.06	0.02	0.13	0.09	0.01	0.01	0.01	0.06	99.62	100.28
230LS1 G1 P2	0.33	0.04	0.05	0.02	0.11	0.01	0.00	0.02	0.08	99.39	99.95
230LS1 G1 P3	0.33	0.01	0.01	0.01	0.05	0.02	0.01	0.01	0.11	99.60	100.16
230LS1 G1 P4	0.32	0.04	0.03	0.01	0.08	0.00	0.00	0.03	0.07	99.77	100.27
230LS1 G1 P5	0.31	0.04	0.05	0.00	0.04	0.01	0.00	0.08	0.05	99.16	99.59
230LS1 G1 P6	0.32	0.04	0.05	0.01	0.04	0.02	0.00	0.09	0.06	100.19	100.62
230LS1 G1 P7	0.35	0.03	0.00	0.04	0.04	0.01	0.00	0.11	0.06	99.39	100.03
230LS1 G1 P8	0.33	0.00	0.04	0.01	0.05	0.02	0.01	0.00	0.10	99.77	100.30
230LS1 G1 P9	0.31	0.02	0.06	0.03	0.05	0.02	0.00	0.09	0.05	98.10	98.57
230LS1 G1 P10	0.16	0.01	0.02	1.51	0.05	0.18	1.71	0.05	0.07	95.65	99.35
230LS1 G1 P11	0.29	0.03	0.06	0.01	0.06	0.03	0.00	0.04	0.08	99.51	100.11
230LS1 G1 P12	0.28	0.01	0.02	0.01	0.05	0.02	0.01	0.02	0.09	98.97	99.42
230LS1 G1 P13	0.35	0.02	0.03	0.02	0.08	0.00	0.01	0.03	0.07	98.57	99.16
230LS1 G4 P1	0.35	0.03	0.00	0.01	0.08	0.03	0.01	0.02	0.07	99.05	99.60
230LS1 G4 P2	0.32	0.04	0.01	0.01	0.04	0.02	0.01	0.01	0.07	99.85	100.32
230LS1 G4 P3	0.25	0.03	0.01	0.01	0.04	0.09	0.00	0.01	0.07	98.75	99.24
230LS1 G4 P4	0.24	0.00	0.00	0.00	0.04	0.01	0.00	0.02	0.06	100.14	100.47
230LS1 G4 P5	0.33	0.01	0.01	0.12	0.08	0.02	0.01	0.09	0.08	98.59	99.15
230LS1 G2 P1	2.88	0.04	0.06	0.01	0.05	0.10	0.00	0.05	0.07	95.72	98.96
230LS1 G2 P2	0.15	0.03	0.01	0.01	0.06	0.06	0.00	0.04	0.08	99.86	100.30
230LS1 G2 P3	0.20	0.05	0.02	0.01	0.07	0.02	0.01	0.04	0.07	100.17	100.51
230LS1 G2 P4	0.18	0.04	0.04	0.01	0.02	0.17	0.00	0.03	0.06	99.69	100.16
230LS1 G2 P5	0.27	0.03	0.01	0.01	0.04	0.01	0.00	0.02	0.08	99.24	99.73
230LS1 G2 P6	0.24	0.02	0.01	0.01	0.05	0.02	0.00	0.02	0.07	99.50	99.91
230LS1 G2 P7	0.35	0.04	0.06	0.01	0.06	0.01	0.00	0.01	0.08	98.48	99.00
230LS1 G2 P8	0.31	0.03	0.02	0.02	0.09	0.01	0.00	0.05	0.08	100.16	100.61
230LS1 G2 P9	0.33	0.03	0.01	0.01	0.05	0.04	0.01	0.02	0.08	99.08	99.61
230LS1 G2 P10	0.34	0.02	0.07	0.01	0.05	0.03	0.00	0.02	0.06	99.43	100.04
230LS1 G2 P11	0.23	0.05	0.03	0.02	0.04	0.02	0.02	0.02	0.05	99.25	99.67
230LS1 G2 P12	0.32	0.06	0.02	0.04	0.05	0.02	0.00	0.04	0.09	99.07	99.69
230LS1 G2 P13	0.27	0.03	0.02	0.01	0.04	0.01	0.00	0.04	0.08	99.87	100.37
230LS1 G2 P14	0.24	0.06	0.02	0.01	0.06	0.03	0.01	0.06	0.07	98.97	99.42
230LS1 G2 P15	3.39	0.03	0.03	0.01	0.07	0.01	0.01	0.02	0.05	96.00	99.60
230LS1 G3 P1	0.17	0.06	0.08	0.01	0.06	0.01	0.00	0.02	0.07	99.54	100.02
230LS1 G3 P2	1.66	0.01	0.03	0.01	0.07	0.04	0.00	0.03	0.07	97.98	99.80
230LS1 G3 P3	0.22	0.03	0.02	0.01	0.06	0.03	0.00	0.06	0.08	99.10	99.57
230LS1 G3 P4	0.22	0.02	0.04	0.01	0.05	0.03	0.01	0.05	0.09	99.71	100.13
230LS1 G3 P5	0.23	0.03	0.00	0.01	0.05	0.08	0.00	0.03	0.08	100.22	100.73
230LS1 G3 P6	0.34	0.02	0.00	0.01	0.05	0.05	0.00	0.06	0.08	99.07	99.68
230LS1 G3 P7	0.27	0.08	0.00	0.09	0.10	0.02	0.00	0.05	0.10	99.14	99.75
230LS1 G3 P8	0.18	0.00	0.01	0.02	0.08	0.02	0.02	0.00	0.06	99.62	99.97
230LS1 G3 P9	0.21	0.06	0.01	0.00	0.06	0.04	0.00	0.09	0.06	98.64	99.14
230LS1 G3 P10	0.22	0.06	0.01	0.01	0.04	0.03	0.01	0.00	0.08	99.74	100.18
230LS1 G3 P11	0.24	0.00	0.05	0.01	0.09	0.03	0.01	0.03	0.06	99.76	100.13
230LS1 G3 P12	0.32	0.03	0.02	0.01	0.03	0.01	0.01	0.01	0.05	99.54	100.04
230LS1 G3 P13	0.36	0.05	0.08	0.08	0.05	0.12	0.01	0.03	0.07	97.09	97.85
230LS1 G5 P1	0.37	0.04	0.02	0.05	0.05	0.02	0.00	0.00	0.08	99.19	99.83
230LS1 G5 P2	0.28	0.05	0.00	0.02	0.06	0.02	0.01	0.10	0.10	99.46	99.89
230LS1 G5 P3	0.21	0.03	0.02	0.00	0.08	0.02	0.01	0.04	0.07	99.47	99.90
230LS1 G5 P4	0.23	0.05	0.03	0.00	0.05	10.76	0.01	0.02	0.08	89.70	100.92
230LS1 G5 P5	0.34	0.04	0.04	0.03	0.05	0.05	0.03	0.01	0.10	99.37	100.03
230LS1 G5 P6	0.34	0.03	0.01	0.01	0.08	0.07	0.00	0.02	0.08	99.70	100.32
230LS1 G5 P7	0.27	0.00	0.03	0.00	0.04	0.02	0.01	0.03	0.07	99.57	99.98
230LS1 G5 P8	0.19	0.04	0.03	0.01	0.09	0.01	0.00	0.00	0.07	100.23	100.68

Table A4 – VIII: Titanite Chemistry.

93LS1																
EPMA wt%	F	FeO	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Total			F	FeO	CaO	SiO ₂	Al ₂ O ₃	TiO ₂	Total
93LS1-R1G3 rim	0.62	0.52	28.04	30.59	2.97	35.67	98.16		93LS1-R5G4	<MDL	0.56	28.41	30.73	1.44	37.96	99.09
93LS1-R1G4	0.48	0.47	28.35	30.68	2.79	36.51	99.07		93LS1-R5G6	0.67	0.52	28.20	30.63	2.81	35.43	97.99
93LS1-R1G5	0.59	0.63	28.02	30.48	2.52	36.38	98.37		93LS1-R5G7	0.50	0.61	27.88	30.30	2.50	36.33	97.91
93LS1-R1G6	0.58	0.62	28.16	30.73	3.19	35.19	98.23		93LS1-R5G8	0.30	0.40	28.47	30.50	1.61	37.62	98.77
93LS1-R1G7	0.35	0.68	28.21	30.55	2.03	36.10	97.77		93LS1-R5G9	0.37	0.62	28.53	30.68	1.73	36.84	98.61
93LS1-R1G8	0.20	0.56	28.30	30.79	1.86	36.62	98.23		93LS1-R6G1	0.55	0.61	28.19	30.73	2.63	36.35	98.84
93LS1-R1G9	0.16	0.28	27.80	30.40	1.14	38.67	98.39		93LS1-R6G2	0.12	0.34	28.18	30.55	1.25	38.95	99.34
93LS1-R1G10	0.52	0.61	28.13	30.66	2.58	36.88	99.15		93LS1-R6G3	0.28	0.61	28.27	30.54	1.74	37.88	99.21
93LS1-R2G1 core	0.45	0.63	28.06	30.55	2.54	36.57	98.61		93LS1-R6G4	0.50	0.57	28.42	30.62	2.22	36.92	99.04
93LS1-R2G1 rim	0.41	0.73	27.93	30.51	2.31	36.36	98.08		93LS1-R6G5	0.50	0.50	28.09	30.67	2.66	35.65	97.85
93LS1-R2G2	0.81	0.60	28.27	30.60	3.12	35.59	98.66		93LS1-R6G6 core	0.57	0.65	28.06	30.43	2.72	35.38	97.57
93LS1-R2G3	0.16	0.31	27.91	30.60	1.16	38.51	98.59		93LS1-R6G6 rim	0.25	0.42	28.29	30.72	1.47	38.26	99.31
93LS1-R2G4	0.66	0.63	28.06	30.50	2.74	35.51	97.81		93LS1-R6G7	0.32	0.40	28.15	30.57	1.40	37.78	98.48
93LS1-R2G5	0.07	0.33	28.31	30.83	1.26	38.46	99.24		93LS1-R6G8	0.41	0.45	28.41	30.64	2.39	37.02	99.15
93LS1-R2G6	0.17	0.38	28.10	30.47	1.15	38.61	98.79		93LS1-R6G9 rim	0.38	0.42	28.21	30.61	1.79	37.60	98.85
93LS1-R2G7	0.39	0.52	28.30	30.74	2.28	36.39	98.46		93LS1-R6G9 core	0.60	0.60	28.24	30.56	2.73	36.44	98.92
93LS1-R2G8	0.56	0.62	28.03	30.54	2.76	36.03	98.31		93LS1-R6G10	0.72	0.68	28.26	30.50	3.15	34.90	97.90
93LS1-R2G9	0.58	0.61	28.25	30.70	2.90	35.67	98.46		93LS1-R7G1	0.22	0.36	28.35	30.70	1.28	37.68	98.50
93LS1-R2G10	0.60	0.68	28.08	30.64	2.52	35.69	97.95		93LS1-R7G2	0.31	0.50	28.15	30.61	1.81	37.15	98.41
93LS1-R3G1	0.20	0.36	28.39	30.44	1.32	38.00	98.62		93LS1-R7G3	0.48	0.65	27.85	30.46	2.65	36.38	98.29
93LS1-R3G2	0.59	0.67	27.94	30.54	2.81	36.42	98.72		93LS1-R7G4	0.19	0.53	28.39	30.71	1.87	37.66	99.27
93LS1-R3G3	0.26	0.38	27.92	30.18	1.90	37.96	98.49		93LS1-R7G5	0.28	0.52	28.16	30.63	1.57	37.69	98.74
93LS1-R3G4	0.53	0.62	28.10	30.72	2.60	36.55	98.89		93LS1-R7G6	0.44	0.50	28.31	30.64	2.18	37.05	98.93
93LS1-R3G5	0.73	0.57	28.52	30.83	2.95	35.19	98.49		93LS1-R7G7	0.74	0.53	28.21	30.66	3.17	35.15	98.15
93LS1-R3G6	0.59	0.63	28.23	30.63	2.87	36.16	98.84		93LS1-R7G8	0.56	0.54	28.32	30.51	2.88	35.52	98.10
93LS1-R3G7	0.31	0.40	28.15	30.37	1.65	37.53	98.27		93LS1-R7G9	0.61	0.54	28.35	30.74	2.81	36.15	98.94
93LS1-R3G8	0.51	0.58	28.01	30.54	2.61	36.04	98.07		93LS1-R7G10	0.55	0.64	28.18	30.60	2.49	35.99	98.21
93LS1-R3G9	2.21	0.06	51.92	-0.04	0.01	0.01	53.22		93LS1-R8G1	0.68	0.56	28.21	30.69	2.84	35.28	97.97
93LS1-R3G10	0.52	0.58	28.12	30.60	2.71	36.25	98.57		93LS1-R8G2 core	0.58	0.64	28.05	30.68	2.97	35.69	98.36
93LS1-R4G1	0.48	0.56	28.17	30.84	2.99	35.57	98.41		93LS1-R8G2 rim	0.59	0.73	27.88	30.17	2.53	36.26	97.90
93LS1-R4G2	0.40	0.43	28.13	30.39	1.64	37.49	98.31		93LS1-R8G3	0.35	0.50	28.28	30.54	2.58	36.37	98.48
93LS1-R4G3 core	0.61	0.61	28.14	30.42	2.61	36.21	98.34		93LS1-R8G4	0.60	0.51	28.30	30.51	2.82	35.92	98.41
93LS1-R4G3 rim	0.31	0.50	28.27	30.74	2.03	36.90	98.61		93LS1-R8G5	0.57	0.57	28.25	30.58	2.96	35.14	97.83
93LS1-R4G4 core	0.58	0.44	28.46	30.72	2.67	35.94	98.56		93LS1-R8G6	0.13	0.39	28.16	30.34	1.28	38.76	99.01
93LS1-R4G4 rim	0.50	0.63	28.12	30.44	2.80	35.83	98.11		93LS1-R8G8	0.63	0.52	28.29	30.81	3.19	35.36	98.54
93LS1-R4G5	0.16	0.40	28.20	30.52	1.73	37.67	98.62		93LS1-R8G10	0.44	0.50	28.13	30.55	2.72	35.97	98.12
93LS1-R4G6	0.21	0.51	28.42	30.82	1.77	36.88	98.52		93LS1-R9G1	0.53	0.55	28.27	30.57	2.88	35.50	98.08
93LS1-R4G7 core	0.51	0.60	28.05	30.45	2.40	36.10	97.90		93LS1-R9G2	0.27	0.40	28.35	30.42	1.57	38.25	99.16
93LS1-R4G7 rim	0.48	0.53	28.28	30.80	2.20	37.63	99.72		93LS1-R9G3	0.75	0.53	28.44	30.71	3.36	35.34	98.82
93LS1-R4G8	0.25	0.40	28.33	30.40	1.46	37.68	98.41		93LS1-R9G4	0.41	0.48	28.28	30.67	2.77	36.17	98.62
93LS1-R4G9	0.58	0.62	28.14	30.63	2.70	35.77	98.20		93LS1-R9G5	0.47	0.65	28.18	30.48	2.42	36.39	98.38
93LS1-R4G10	0.61	0.56	28.27	30.70	3.16	35.27	98.31		93LS1-R9G6	0.37	0.50	28.03	30.28	1.72	37.60	98.33
93LS1-R5G1	0.12	0.55	28.24	30.67	1.72	38.19	99.45		93LS1-R9G7	0.47	0.67	28.44	30.93	2.78	35.53	98.62
93LS1-R5G2	0.65	0.64	28.15	30.67	2.98	35.56	98.38		93LS1-R9G8	0.25	0.43	28.10	30.53	1.41	36.62	97.23
93LS1-R5G3	0.31	0.53	28.43	30.58	1.93	37.94	99.60		93LS1-R9G10	0.57	0.56	28.16	30.58	2.44	36.81	98.88
93LS1-R9G11 rim	0.58	0.62	28.23	30.73	2.79	36.10	98.79		93LS1-R9G11 cor	0.48	0.49	28.38	30.57	2.28	36.64	98.64

Table A4 – IX: Apatite Chemistry.

183LS1												
EPMA wt%	F	P ₂ O ₅	Cl	CaO	Total			F	P ₂ O ₅	Cl	CaO	Total
183LS1-R1G1	2.05	42.09	0.05	55.41	98.72	183LS1-R5G4		1.36	42.10	0.06	54.78	97.71
183LS1-R1G2A	1.71	41.74	0.07	55.19	97.99	183LS1-R5G5		1.56	42.23	0.06	54.78	97.97
183LS1-R1G2B	1.89	42.68	0.06	55.67	99.49	183LS1-R5G6		1.45	42.28	0.06	54.59	97.77
183LS1-R1G3	1.51	42.21	0.04	55.12	98.23	183LS1-R5G7		1.66	42.41	0.05	55.03	98.44
183LS1-R1G4A	1.56	42.24	0.05	54.94	98.13	183LS1-R5G9		1.78	42.31	0.04	55.28	98.65
183LS1-R1G4B	1.49	42.11	0.06	54.97	97.99	183LS1-R5G10A		1.54	42.32	0.06	54.71	97.96
183LS1-R1G5	1.61	42.25	0.05	54.82	98.04	183LS1-R5G10B		1.59	42.18	0.06	54.81	97.97
183LS1-R1G6	1.84	41.98	0.04	54.69	97.77	183LS1-R6G1		1.53	41.97	0.06	54.68	97.58
183LS1-R1G7	1.64	42.35	0.01	55.30	98.61	183LS1-R6G2		1.62	42.20	0.04	54.74	97.91
183LS1-R1G8	1.47	42.21	0.06	54.82	97.93	183LS1-R6G4		1.58	42.07	0.05	54.78	97.81
183LS1-R1G9A	1.62	41.92	0.05	54.94	97.83	183LS1-R6G5		1.59	42.05	0.05	54.70	97.71
183LS1-R1G9B	1.43	42.30	0.05	54.92	98.09	183LS1-R6G6		1.64	42.33	0.04	55.03	98.34
183LS1-R1G10	1.63	42.13	0.05	54.90	98.00	183LS1-R6G7		1.94	42.49	0.05	55.31	98.96
183LS1-R2G1	1.56	42.15	0.04	54.92	98.00	183LS1-R6G8		1.80	42.14	0.05	54.89	98.12
183LS1-R2G2	1.60	42.33	0.05	55.19	98.48	183LS1-R6G9		0.22	0.08	0.00	28.79	29.00
183LS1-R2G3	1.87	42.57	0.03	55.88	99.57	183LS1-R7G2		1.51	42.27	0.06	55.15	98.34
183LS1-R2G4	1.60	42.34	0.05	54.81	98.11	183LS1-R7G3B		1.56	42.03	0.05	54.70	97.66
183LS1-R2G5	1.63	41.86	0.04	54.57	97.41	183LS1-R7G3A		1.60	42.48	0.04	54.90	98.35
183LS1-R2G6	1.63	42.08	0.04	55.26	98.32	183LS1-R7G4		1.32	42.08	0.06	55.02	97.91
183LS1-R2G7	1.57	42.19	0.05	55.01	98.15	183LS1-R7G5		1.84	41.77	0.02	55.22	98.07
183LS1-R2G8	1.95	41.87	0.04	55.19	98.22	183LS1-R7G6		1.46	42.12	0.07	55.01	98.03
183LS1-R2G9	1.41	38.05	0.10	50.27	89.22	183LS1-R7G8		1.49	42.43	0.06	55.34	98.68
183LS1-R2G10	1.51	42.17	0.04	55.02	98.10	183LS1-R7G10		1.40	41.85	0.05	54.83	97.53
183LS1-R3G1	1.59	42.13	0.06	54.83	97.92	183LS1-R8G1		1.97	42.72	0.04	55.16	99.05
183LS1-R3G2	1.51	41.70	0.05	55.11	97.72	183LS1-R8G3		1.55	42.37	0.04	54.99	98.29
183LS1-R3G3	1.58	42.02	0.04	54.90	97.87	183LS1-R8G4		1.79	42.42	0.04	55.10	98.59
183LS1-R3G4A	1.93	41.88	0.05	55.38	98.41	183LS1-R8G5		1.45	42.40	0.06	54.80	98.08
183LS1-R3G4B	1.71	42.35	0.06	55.09	98.47	183LS1-R8G6		0.15	0.10	-0.01	28.75	28.93
183LS1-R3G5A	1.72	42.43	0.04	54.77	98.23	183LS1-R8G7		1.44	41.75	0.07	54.48	97.12
183LS1-R3G5B	2.05	42.20	0.01	55.03	98.43	183LS1-R8G8		1.47	42.06	0.06	54.99	97.94
183LS1-R3G8	1.61	41.76	0.05	54.74	97.47	183LS1-R8G9		1.93	42.27	0.03	55.60	99.01
183LS1-R3G9	1.37	41.88	0.07	54.60	97.32	183LS1-R8G10A		1.42	42.11	0.07	55.03	98.02
183LS1-R3G10	1.51	41.82	0.05	54.86	97.59	183LS1-R8G10B		1.54	42.21	0.06	54.66	97.80
183LS1-R4G1	1.66	41.99	0.04	54.85	97.83	183LS1-R9G2B		1.56	42.01	0.05	55.02	97.97
183LS1-R4G2	1.53	42.40	0.05	54.85	98.17	183LS1-R9G2A		1.60	41.88	0.05	54.69	97.53
183LS1-R4G3	1.47	42.25	0.07	54.64	97.79	183LS1-R9G3A		1.56	42.49	0.04	54.73	98.16
183LS1-R4G4	1.85	42.22	0.06	55.33	98.66	183LS1-R9G3B		1.56	42.03	0.04	54.95	97.91
183LS1-R4G5	1.36	42.03	0.07	54.71	97.58	183LS1-R9G4		1.58	42.39	0.05	54.90	98.24
183LS1-R4G6B	1.42	42.49	0.07	54.83	98.19	183LS1-R9G5		1.40	42.23	0.05	54.63	97.71
183LS1-R4G6A	1.52	41.96	0.05	55.04	97.91	183LS1-R9G6		1.56	41.90	0.04	54.72	97.56
183LS1-R4G7	1.49	42.17	0.05	54.85	97.92	183LS1-R9G8		1.51	42.00	0.06	55.11	98.02
183LS1-R4G8A	1.64	42.40	0.06	55.24	98.63	183LS1-R9G9		0.11	0.09	0.00	28.62	28.77
183LS1-R4G8B	1.58	42.08	0.06	54.91	97.96	183LS1-R9G10		1.69	42.42	0.05	55.32	98.76
183LS1-R4G9	2.08	41.48	0.03	55.18	97.89	183LS1-R10G1		0.10	0.13	0.00	28.45	28.65
183LS1-R4G10	1.61	42.56	0.03	55.69	99.20	183LS1-R10G2		1.49	41.98	0.04	54.53	97.41
183LS1-R5G1	1.49	41.86	0.06	54.62	97.38	183LS1-R10G3		0.13	0.14	0.00	28.46	28.68
183LS1-R5G2A	1.45	42.38	0.06	54.74	98.00	183LS1-R10G6		1.61	41.86	0.04	54.90	97.72
183LS1-R5G2B	1.45	42.31	0.05	54.94	98.13	183LS1-R10G7		1.63	42.00	0.06	54.64	97.63
183LS1-R5G3	1.74	42.34	0.04	54.92	98.30	183LS1-R10G8		1.56	42.03	0.04	54.62	97.59
183LS1-R10G10	1.49	42.01	0.06	54.71	97.63	183LS1-R10G9		1.83	42.14	0.04	55.27	98.50

Appendix A5: LA-ICPMS Trace Elements and U-Pb analysis

Table A5 – I: Rutile trace elements and U-Pb analysis.

93LS1																	
Sample Grain #	Sc ppm	V ppm	Cr ppm	Y ppm	Zr ppm	Nb ppm	Mo ppm	Sn ppm	Sb ppm	Hf ppm	Ta ppm	W ppm	U ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
93LS1 R5G1	2.02	1995	74.8	L.O.D.	123	408	10.9	39.9	1.68	3.76	33.6	4.23	3.74	15.1515	4.90	0.1300	0.10
93LS1 R5G1	2.52	2004	78.4	L.O.D.	128	393	16.9	39.1	1.82	4.90	22.6	4.56	3.55	11.9048	2.10	0.1250	0.08
93LS1 R8G6	2.26	1960	80.1	0.01	113	411	16.1	46.0	2.31	4.40	29.9	4.30	2.82	12.6582	2.30	0.0940	0.04
93LS1 R8G9	2.47	1853	82.5	0.03	166	412	16.0	40.2	1.58	6.40	25.0	4.27	3.14	10.8696	2.10	0.1130	0.04
93LS1 R7G5	2.15	1725	84.2	0.00	127	393	13.8	42.4	1.67	3.58	23.2	4.13	3.14	9.4340	2.00	0.1000	0.03
93LS1 R8G8	2.35	1773	86.6	0.04	176	408	15.1	38.3	2.13	6.11	30.9	3.93	3.89	12.1951	2.20	0.1200	0.10
93LS1 R6G9	2.00	1861	87.0	0.04	157	417	14.9	40.5	2.28	4.14	31.7	4.39	3.52	10.9890	2.40	0.1900	0.17
93LS1 R2G6	1.75	1835	87.0	L.O.D.	202	387	16.4	43.3	1.93	5.40	18.9	4.05	2.23	10.2041	1.40	0.1300	0.07
93LS1 R8G8	2.78	1757	88.6	0.54	410	413	15.2	39.2	1.43	12.2	26.2	3.53	3.29	11.9048	2.00	0.1260	0.07
93LS1 R4G4	2.06	1730	91.7	0.39	288	388	15.1	36.9	1.62	8.50	21.1	4.10	3.50	12.7714	2.20	0.1080	0.05
93LS1 R1G10	1.83	1926	93.8	L.O.D.	184	421	9.4	40.2	2.46	7.06	28.9	4.34	4.47	15.0376	2.80	0.1110	0.05
93LS1 R7G4	2.46	1859	95.8	0.88	338	408	16.0	41.1	1.75	10.1	25.3	3.64	4.04	13.3333	2.60	0.1180	0.07
93LS1 R6G1	2.44	2029	96.2	L.O.D.	97.4	405	14.4	43.8	1.79	3.73	25.3	4.77	3.36	12.1951	2.40	0.1500	0.11
93LS1 R1G9	2.14	1896	96.7	L.O.D.	129	411	15.4	41.9	2.10	5.16	25.8	5.12	4.04	11.6279	1.70	0.0980	0.04
93LS1 R4G9	3.91	1693	99.0	0.51	1010	398	15.6	38.1	1.61	30.0	21.4	4.67	3.74	13.1579	2.50	0.0820	0.03
93LS1 R7G8	1.98	1814	101	0.01	136	398	12.2	43.3	2.12	5.56	27.2	4.50	2.79	9.0090	2.90	0.2400	0.14
93LS1 R6G2	2.12	1954	101	L.O.D.	172	414	13.4	40.1	3.42	6.81	27.7	4.60	1.84	10.0000	2.20	0.0650	0.05
93LS1 R4G2	2.02	1829	102	L.O.D.	103	410	15.1	42.7	1.89	3.30	25.5	4.34	4.16	14.8810	2.90	0.0980	0.04
93LS1 R3G10	2.00	1815	103	L.O.D.	199	413	15.3	42.2	2.26	6.40	23.5	4.54	3.58	11.8624	1.90	0.1110	0.08
93LS1 R3G8	2.84	1649	104	0.22	560	404	11.2	39.2	1.40	14.5	22.0	4.39	4.00	14.0845	2.00	0.0900	0.03
93LS1 R6G6	2.69	1898	108	0.19	420	392	16.0	42.9	1.85	11.4	20.3	4.54	3.59	10.7527	2.10	0.1130	0.04
93LS1 R2G1	1.74	1977	108	L.O.D.	119	406	17.0	41.9	2.15	4.26	22.2	4.29	2.60	9.6154	1.70	0.1270	0.09
93LS1 R5G9	2.22	1825	109	L.O.D.	157	420	12.8	41.3	3.71	4.92	27.1	5.77	3.63	11.2360	2.10	0.1370	0.07
93LS1 R5G10	1.61	1908	110	L.O.D.	146	402	16.4	40.0	1.61	4.06	24.1	4.44	3.80	11.7647	2.30	0.2400	0.16
93LS1 R9G6	1.36	1948	110	0.08	154	415	12.9	37.1	2.13	5.02	26.8	4.86	3.94	14.2857	2.60	0.1570	0.08
93LS1 R6G3	1.88	1864	111	L.O.D.	114	396	16.5	39.0	2.42	4.14	24.7	4.95	1.76	9.7087	1.90	0.1140	0.09
93LS1 R3G4	3.91	2026	115	0.62	930	417	14.6	40.8	2.20	24.8	26.8	4.42	4.39	12.5000	1.60	0.1050	0.04
93LS1 R1G8	2.06	1953	118	L.O.D.	318	393	10.7	39.4	4.49	9.40	20.1	4.90	2.87	9.9010	2.20	0.0870	0.05
93LS1 R4G3	1.37	1918	120	L.O.D.	100	390	16.4	41.9	2.23	3.57	21.1	5.29	2.50	9.6154	3.90	0.1300	0.13
93LS1 R5G7	1.79	2050	121	L.O.D.	137	392	16.3	41.7	4.27	5.68	13.4	4.57	1.37	8.6207	2.40	0.1700	0.12
93LS1 R9G2	2.10	1733	126	L.O.D.	104	411	17.5	40.7	2.24	4.24	25.8	4.80	3.58	14.7711	2.30	0.1290	0.05
93LS1 R4G6	1.87	1848	130	L.O.D.	164	387	15.3	41.5	2.29	5.20	23.1	4.48	3.28	10.1010	2.10	0.1420	0.06
93LS1 R2G7	0.01	1730	133	0.15	189	412	14.1	37.0	3.36	6.20	21.1	3.90	1.75	10.7527	2.60	0.0900	0.10
93LS1 R3G1	1.94	2069	157	L.O.D.	165	413	15.8	45.7	2.96	5.84	25.8	4.32	3.00	10.5263	3.00	0.0910	0.05
93LS1 R1G6	2.07	1742	180	L.O.D.	233	417	8.2	34.8	5.16	8.20	27.7	4.17	2.60	8.7719	2.90	0.1380	0.09

Table A5 – I: (Continued)

Sample Grain #	Sc ppm	V ppm	Cr ppm	Y ppm	Zr ppm	Nb ppm	Mo ppm	Sn ppm	Sb ppm	Hf ppm	Ta ppm	W ppm	U ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
93LS1 R6G5	1.23	1811	91	0.01	95.3	389	17.5	42.8	2.74	3.28	20.2	4.20	2.22	7.8740	2.50	0.0930	0.06
93LS1 R1G1	1.98	1902	112	L.O.D.	271	409	11.6	38.5	2.57	6.80	22.5	4.89	4.26	12.9870	2.60	0.0760	0.02
93LS1 R2G9	2.31	1889	126	L.O.D.	301	395	16.5	45.0	2.15	9.00	24.0	3.91	4.28	11.2360	2.00	0.0510	0.02
93LS1 R1G4	2.24	2012	102	L.O.D.	104	404	18.6	45.6	1.86	3.33	23.7	5.03	3.30	9.0090	1.90	0.0610	0.03
93LS1 R3G6	1.73	2018	109	L.O.D.	147	395	16.4	44.7	2.43	5.62	15.0	3.84	4.51	11.7647	1.80	0.0780	0.03
93LS1 R1G5	1.89	1753	87	L.O.D.	135	375	14.8	41.7	1.74	4.09	18.2	4.09	4.30	12.9870	1.70	0.0540	0.03
93LS1 R6G8	2.00	1933	112	0.06	183	398	16.0	38.0	2.81	5.50	23.0	4.51	2.13	8.9286	3.10	0.0860	0.07
93LS1 R0G1	1.92	1898	129	L.O.D.	236	422	9.7	42.4	2.28	7.90	21.9	3.96	4.65	13.3333	2.10	0.0570	0.03
93LS1 R7G10	1.79	1834	102	L.O.D.	146	369	12.9	42.2	2.67	5.33	16.8	4.11	3.19	9.6154	1.60	0.0640	0.03
93LS1 R5G6	1.89	1712	120	L.O.D.	195	400	14.9	40.6	3.51	7.88	25.7	4.70	3.99	14.5985	1.80	0.0530	0.04
93LS1 R2G4	2.42	1601	98	L.O.D.	229	396	13.5	41.6	2.12	7.20	23.4	4.60	4.17	10.8696	1.40	0.0680	0.03
93LS1 R5G%	2.09	1912	97	L.O.D.	260	405	16.7	38.8	2.08	6.90	30.6	4.35	2.15	7.8125	2.90	0.1010	0.08
93LS1 R2G8	2.58	1790	109	L.O.D.	290	384	16.4	43.1	2.01	11.5	25.4	4.13	3.96	10.7527	2.00	0.0660	0.03
93LS1 R8G7	2.04	1830	117	0.15	199	389	15.7	42.8	1.98	6.10	23.0	4.03	3.76	9.6154	3.00	0.0940	0.03
93LS1 R5G4	1.99	1945	105	L.O.D.	149	411	15.4	43.2	3.40	4.92	21.1	4.99	1.18	11.4943	7.60	0.1200	0.14
Data discarded for zircon contamination																	
93LS1 R4G1	16.20	1738	99	9.70	7490	366	12.4	32.2	5.06	199	19.4	5.28	4.21	9.7087	2.00	0.0490	0.03
93LS1 R9G1	2.11	1804	112	0.03	108	413	12.8	36.9	6.30	4.30	22.8	4.83	0.33	0.2857	3.60	0.2100	0.29
93LS1 R9G3	2.73	1872	113	0.73	490	430	10.7	34.2	6.00	15.4	20.4	5.43	0.62	9.4340	7.50	0.7000	0.78
93LS1 R9G5	2.20	1920	104	0.09	222	396	11.6	35.9	3.78	6.80	16.2	4.13	1.04	11.6279	15.00	0.8800	0.80
93LS1 R4G9	14.20	1708	103	L.O.D.	5500	398	15.6	40.9	2.12	149	20.8	3.94	4.67	11.9048	1.50	0.1440	0.05
93LS1 R5G10	3.66	1905	118	0.29	620	399	11.2	42.3	2.16	16.10	20.6	4.61	3.61	10.3093	2.30	0.3900	0.33
93LS1 R7G7	4.10	1993	130	0.83	1070	408	9.2	34.3	7.63	29.0	20.1	5.82	0.50	11.9048	16.00	0.2800	0.23
93LS1 R7G3	3.82	1846	93	0.48	840	408	10.2	30.7	7.92	22.1	21.2	5.88	0.28	7.1429	7.40	0.3900	0.21
93LS1 R2G3	14.10	1951	103	2.50	5500	405	13.0	36.8	6.00	155	26.4	4.84	2.26	6.0606	1.60	0.5800	0.25
93LS1 R8G10	30.00	1890	95	2.60	10500	398	15.2	45.0	4.30	260	23.2	5.60	6.10	0.3891	2.00	0.6000	0.11
93LS1 R7G3	3.70	1814	90	0.92	910	385	13.7	42.9	2.54	24.4	23.8	4.53	2.29	8.4746	2.00	0.1900	0.15
93LS1 R8G3	6.20	1861	126	0.78	1850	386	14.2	40.7	2.01	50.0	20.8	3.91	4.13	12.1951	2.40	0.1160	0.06
93LS1 R1G7	6.10	1741	110	0.47	2120	392	13.8	43.2	2.20	58.0	21.2	5.07	4.48	12.6582	2.30	0.1270	0.04
93LS1 R5G3	11.00	1939	107	1.85	4300	406	15.1	41.7	1.94	111	20.0	4.41	2.75	9.6154	2.40	0.1340	0.07
93LS1 R4G3	10.10	1927	124	1.55	4500	398	13.4	43.3	2.96	122	21.4	4.57	4.60	10.1010	1.20	0.0510	0.03
93LS1 R3G3	0.01	1557	76	L.O.D.	128	397	15.6	37.9	2.05	4.07	21.4	4.27	2.85	8.6957	2.40	0.1390	0.10
93LS1 R7G9	3.38	1724	104	0.44	348	389	14.5	42.2	2.47	11.6	21.5	3.54	4.03	13.6986	2.40	0.0720	0.03
93LS1 R8G2	2.10	1652	91	-0.01	125	375	16.5	38.7	2.12	4.41	21.7	4.30	3.12	15.7233	4.10	0.0870	0.05
93LS1 R8G1	1.93	1700	87	0.00	96.7	400	16.6	39.7	2.85	3.80	24.5	4.60	2.96	10.2041	2.00	0.2100	0.15

Table A5 – I: (Continued)

Sample Grain #	Sc ppm	V ppm	Cr ppm	Y ppm	Zr ppm	Nb ppm	Mo ppm	Sn ppm	Sb ppm	Hf ppm	Ta ppm	W ppm	U ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
93LS1 R7G1	87.00	1492	83	46.40	31300	401	12.2	38.0	8.30	833	23.2	5.10	15.40	12.0192	1.50	0.0630	0.02
93LS1 R7G2	2.64	1938	111	0.22	600	513	7.6	30.0	10.4	18.60	26.4	8.48	0.50	3.3333	9.10	0.3600	0.50
93LS1 R8G1	1.88	1885	145	1.04	123	456	10.6	32.8	5.33	4.85	29.4	6.20	0.71	3.1250	9.30	0.2400	0.22
93LS1 R8G5	2.54	1956	106	0.19	320	437	9.3	33.5	8.66	10.5	19.4	5.48	0.35	6.6667	11.00	0.8800	1.53
93LS1 R4G5	2.03	1840	102	0.24	440	405	12.5	37.4	5.12	12.4	24.9	5.06	1.10	14.4928	27.00	1.1000	1.10
93LS1 R2G10	2.37	2020	103	0.35	300	429	13.4	40.3	5.08	9.80	25.6	5.41	0.55	4.1667	28.00	0.1200	1.07
93LS1 R3G2	2.45	1886	92	0.22	370	432	12.4	39.3	6.82	12.5	28.5	4.95	0.35	7.1429	5.30	0.1800	0.17
Data discarded for large errors																	
93LS1 R6G1	2.00	2044	101	L.O.D.	174	404	11.5	39.9	3.59	6.40	23.3	4.54	2.49	10.4167	2.70	0.3800	0.57
93LS1 R7G1	1.75	1602	89	1.21	400	552	10.9	27.0	10.1	12.7	28.0	13.20	0.46	5.4945	5.20	0.3800	0.28
93LS1 R1G2	1.97	1879	136	L.O.D.	147	416	11.1	43.0	5.27	7.00	28.6	4.75	1.27	6.4516	4.80	0.4300	0.31
93LS1 R3G7	1.65	1868	108	L.O.D.	94.5	429	13.4	37.2	6.12	3.74	22.6	5.74	1.30	7.5758	5.30	0.3600	0.34
93LS1 R1G3	L.O.D.	1896	110	L.O.D.	139	446	10.8	40.8	4.63	5.53	22.2	5.24	1.46	8.9286	9.40	0.3100	0.28
93LS1 R3G5	1.70	1887	122	L.O.D.	108	402	14.1	41.5	3.36	3.79	20.6	4.49	1.10	12.6582	77.00	0.1500	0.31
93LS1 R2G5	1.67	1935	120	L.O.D.	149	401	16.1	41.1	4.06	6.15	18.9	4.78	0.98	5.3476	7.10	0.7800	0.86

Table A5 – I: (Continued)

152LS1																		
Sample Grain #	Sc ppm	V ppm	Cr ppm	Y ppm	Zr ppm	Nb ppm	Mo ppm	Sn ppm	Sb ppm	Hf ppm	Ta ppm	W ppm	U ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE	
152-LS1B 1_3	L.O.D.	L.O.D.	70.5	L.O.D.	203	376	10.6	35.1	5.41	L.O.D.	25.7	6.36	4.33	12.75510	1.20	0.15000	0.10	
152LS1 R1 G1	1.41	1907	258	L.O.D.	94	301	17.7	28.4	2.05	0.62	11.0	1.06	2.72	11.49425	2.30	0.09500	0.04	
152LS1 R2 G4	2.09	1784	233	L.O.D.	154	337	14.0	27.7	1.61	0.75	10.2	1.46	1.67	12.82051	2.60	0.13000	0.13	
152-LS1B 3_7	L.O.D.	L.O.D.	17.6	L.O.D.	198	367	12.4	41.4	7.00	L.O.D.	27.1	7.45	3.58	12.34568	2.60	0.10900	0.05	
152-LS1B 4_1	L.O.D.	L.O.D.	52.5	L.O.D.	179	347	10.7	35.1	6.52	L.O.D.	23.6	6.51	3.31	13.42282	1.70	0.07600	0.03	
152LS1 R3 G6	2.60	2071	301	L.O.D.	199	426	12.0	39.9	6.32	1.10	26.7	7.50	3.27	13.88889	2.20	0.04500	0.02	
152-LS1B 5_1	L.O.D.	L.O.D.	238	L.O.D.	179	342	11.5	33.9	6.54	L.O.D.	16.5	6.80	1.77	13.69863	2.60	0.15000	0.16	
152LS1 R4 G2	1.81	1840	205	L.O.D.	175	325	12.4	35.3	3.95	0.75	10.9	1.77	3.29	13.19261	1.70	0.08800	0.03	
152LS1 R1 G3	2.18	1947	230	L.O.D.	185	393	12.9	39.7	3.59	0.83	21.3	6.06	2.64	13.69863	2.50	0.11700	0.08	
152-LS1B 7_4	L.O.D.	L.O.D.	270	L.O.D.	191	356	10.7	37.6	8.50	L.O.D.	24.9	6.90	2.57	8.84956	2.70	0.12000	0.07	
152-LS1B 7_5	2.38	1927	211	L.O.D.	137	365	13.4	35.8	2.41	0.53	12.8	1.75	3.07	11.11111	1.70	0.03900	0.03	
152-LS1B 7_2	L.O.D.	L.O.D.	265	L.O.D.	199	358	11.3	35.6	5.28	L.O.D.	25.9	7.25	4.02	13.36898	1.60	0.11800	0.07	
152-LS1B 1_1	L.O.D.	L.O.D.	70.8	L.O.D.	208	380	13.3	38.5	5.88	L.O.D.	27.7	7.02	3.94	12.04819	1.60	0.11400	0.07	
152LS1 R1 G4	2.04	1940	252	0.07	174	367	11.6	39.6	6.50	0.98	26.2	5.90	2.49	10.20408	3.00	0.09100	0.07	
152LS1 R10 G4	2.21	1932	243	0.08	205	397	15.8	40.2	6.25	1.10	15.4	5.97	2.24	11.49425	1.80	0.05200	0.03	
152LS1 R1 G9	2.01	1845	241	L.O.D.	126	304	17.0	32.7	3.76	0.55	11.6	1.35	1.54	10.00000	2.90	0.05900	0.06	
Data discarded for discordance																		
152LS1 R6 G9	2.66	1905	271	L.O.D.	177	394	16.2	35.4	4.31	0.78	22.3	4.90	1.84	8.06452	2.90	0.19100	0.06	
152-LS1B 3_2	L.O.D.	L.O.D.	16.6	L.O.D.	190	369	11.3	36.0	6.64	L.O.D.	22.0	5.93	3.42	12.23990	1.50	0.18000	0.11	
152LS1 R3 G3	1.71	1877	234	L.O.D.	159	359	16.9	34.4	2.11	0.74	12.6	1.27	3.95	10.41667	1.90	0.20100	0.07	
152-LS1B 1_2	L.O.D.	L.O.D.	12.7	L.O.D.	171	379	9.4	36.8	6.61	L.O.D.	26.6	7.82	2.69	7.81250	1.80	0.32000	0.06	
152-LS1B 7_3	L.O.D.	L.O.D.	245	L.O.D.	183	360	9.3	38.5	6.58	L.O.D.	24.6	7.10	3.79	10.30928	1.70	0.25200	0.07	
152LS1 R2 G6	2.09	1836	217	L.O.D.	154	409	11.2	39.8	2.77	0.92	18.1	1.85	2.32	8.33333	1.90	0.25700	0.09	
152LS1 R1 G5	2.01	2046	250	L.O.D.	181	375	10.7	39.8	4.56	0.69	30.6	7.12	3.17	5.31915	1.80	0.30000	0.10	
152-LS1B 3_3	L.O.D.	L.O.D.	11.9	L.O.D.	163	358	13.0	38.3	5.09	L.O.D.	15.6	6.80	3.98	2.77778	1.40	0.49600	0.08	
152LS1 R2 G9	2.49	1870	261	L.O.D.	174	359	13.4	41.8	2.78	0.79	15.6	5.20	2.74	10.63830	2.90	0.35000	0.23	
152LS1 R3 G4	1.91	1897	212	L.O.D.	172	355	13.1	34.9	4.19	0.68	9.9	2.44	2.33	4.90196	1.50	0.42000	0.10	
152-LS1B 3_1	L.O.D.	L.O.D.	31.9	L.O.D.	149	354	11.2	35.6	7.51	L.O.D.	21.8	6.80	2.57	7.29927	1.20	0.42000	0.12	
152-LS1B 7b_1	L.O.D.	L.O.D.	240	L.O.D.	153	343	8.2	36.0	7.16	L.O.D.	23.9	7.05	0.81	1.69492	0.94	0.83000	0.23	
152LS1 R4 G7	4.43	1793	217	0.33	144	380	13.3	31.9	6.29	0.92	11.5	4.97	0.36	0.00508	0.00	0.82000	0.04	
152LS1 R7 G7	1.82	1809	241	0.17	137	339	13.0	33.3	7.63	0.59	6.9	3.00	0.47	0.00885	0.00	0.67500	0.02	
152LS1 R7 G9	1.88	2003	255	L.O.D.	160	379	11.9	35.6	6.02	0.65	11.7	3.71	0.70	0.01852	0.01	0.73500	0.06	
152LS1 R8 G9	1.84	2015	264	L.O.D.	172	289	15.4	31.2	2.96	0.73	7.5	1.90	0.55	0.02564	0.01	0.78400	0.08	
152LS1 R7 G4	2.36	2106	278	L.O.D.	181	374	13.0	36.2	5.42	0.57	12.2	3.07	0.73	0.03650	0.01	0.68000	0.04	
152LS1 R1 G6	2.18	2066	253	L.O.D.	170	369	13.2	38.4	6.65	0.94	14.1	3.48	0.75	0.03846	0.12	0.88000	0.05	
152LS1 R10 G6	1.99	1950	232	0.09	172	522	13.4	40.1	5.37	1.10	55.1	9.80	0.78	0.40000	2.40	0.61000	0.13	
152LS1 R15 G2	2.50	1929	313	L.O.D.	150	331	14.0	38.1	6.77	0.92	6.9	2.17	0.36	0.05000	0.18	0.94500	0.08	

Table A5 – I: (Continued)

Data discarded for deviation from weighted average																	
Sample Grain #	Sc ppm	V ppm	Cr ppm	Y ppm	Zr ppm	Nb ppm	Mo ppm	Sn ppm	Sb ppm	Hf ppm	Ta ppm	W ppm	U ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
152-LS1B 2_1	L.O.D.	L.O.D.	60.0	L.O.D.	164	376	13.4	35.0	5.61	L.O.D.	24.5	7.51	2.49	0.24155	0.03	0.84000	0.02
152LS1 R5 G10	1.75	1874	268	0.10	141	191	17.1	25.0	1.91	0.45	6.1	1.01	2.57	0.37037	0.37	0.85000	0.21
152LS1 R7 G3	2.48	1948	247	L.O.D.	200	427	13.5	32.9	4.07	0.79	29.7	5.85	2.87	15.72327	2.20	0.02800	0.02
152-LS1B 2_7	L.O.D.	L.O.D.	102	L.O.D.	191	380	10.9	38.0	7.08	L.O.D.	26.0	7.82	3.57	9.17431	1.50	0.08100	0.04
152LS1 R7 G1	2.23	1825	250	L.O.D.	108	296	16.5	31.4	1.43	0.59	11.2	1.23	2.88	9.52381	1.60	0.07500	0.04
152-LS1B 2_5	L.O.D.	L.O.D.	132	L.O.D.	174	386	10.0	39.7	7.09	L.O.D.	24.3	7.30	3.41	6.02410	1.60	0.15000	0.05
152-LS1B 5_2	L.O.D.	L.O.D.	257	L.O.D.	158	364	9.8	33.4	7.46	L.O.D.	15.9	6.00	1.18	5.78035	0.97	0.39000	0.11
152-LS1B 5_3	L.O.D.	L.O.D.	240	L.O.D.	178	348	7.4	28.7	5.29	L.O.D.	24.3	6.87	2.66	12.34568	3.00	0.27900	0.07
Data discarded for large errors																	
152LS1 R8 G2	3.47	2386	61.1	1.17	236	383	14.9	36.5	5.93	0.77	29.7	7.42	4.73	8.13008	1.32	2.70000	2.80
152LS1 R8 G1	1.84	1716	212	L.O.D.	152	410	16.1	29.0	1.88	0.92	13.7	0.68	3.49	15.38462	3.10	0.03100	0.02
152LS1 R10 G9	2.03	1805	253	0.04	153	385	15.6	39.0	3.03	0.54	10.9	1.50	3.67	12.65823	3.20	0.10500	0.05
152LS1 R6 G10	1.76	1765	232	L.O.D.	119	406	13.7	29.9	1.91	0.65	19.0	42.90	2.98	14.49275	3.80	0.03200	0.03
152-LS1B 2_4	L.O.D.	L.O.D.	118	L.O.D.	140	374	9.6	39.7	7.60	L.O.D.	24.4	7.40	1.73	6.09756	1.60	0.65000	0.26
152-LS1B 7_1	L.O.D.	L.O.D.	239	L.O.D.	144	350	10.8	31.0	6.50	L.O.D.	12.5	5.50	1.60	9.70874	2.60	0.44000	0.31
152LS1 R2 G2	2.13	1838	221	L.O.D.	108	340	13.6	29.5	1.70	0.50	8.2	0.31	3.11	12.98701	3.50	0.06000	0.03
152-LS1B 2_3	L.O.D.	L.O.D.	114	L.O.D.	184	396	9.7	37.1	6.65	L.O.D.	24.9	7.60	3.91	12.04819	3.30	0.07500	0.06
152LS1 R5 G5	2.35	1907	254	L.O.D.	188	387	11.7	38.7	5.87	0.87	20.8	5.60	2.67	10.30928	3.20	0.07600	0.03
152LS1 R8 G5	2.06	1681	236	L.O.D.	204	336	12.9	37.2	3.95	1.20	15.5	4.58	2.24	13.33333	4.20	0.06900	0.04
152LS1 R4 G10	2.48	1788	238	L.O.D.	183	386	13.6	33.0	2.71	0.91	16.1	4.41	2.74	15.38462	5.30	0.08800	0.03
152-LS1B 2_2	L.O.D.	L.O.D.	116	L.O.D.	166	434	15.4	44.3	8.40	L.O.D.	31.5	7.20	4.83	14.28571	5.50	0.13600	0.06
152LS1 R9 G10	2.33	2099	259	0.28	168	368	14.7	39.9	5.82	1.00	18.1	5.48	0.76	2.77778	1.08	3.40000	1.70
152LS1 R6 G3	2.35	2263	266	L.O.D.	186	371	10.9	38.8	3.36	0.43	17.6	8.20	3.92	4.08163	1.62	6.40000	9.30
152LS1 R8 G4	2.29	1963	242	L.O.D.	173	416	16.7	35.9	4.37	0.50	29.8	2.48	1.91	0.03571	0.02	5.80000	7.50
152LS1 R4 G9	2.14	2036	299	0.16	144	380	13.8	37.3	4.77	0.91	11.5	2.69	0.88	1.03093	0.48	5.10000	4.70
152LS1 R8 G10	2.44	1971	231	L.O.D.	128	334	15.1	33.1	2.01	0.53	9.5	3.57	3.22	0.61350	0.29	2.30000	2.40
152LS1 R9 G9	2.73	1448	247	L.O.D.	165	330	14.8	26.5	4.67	0.50	9.8	1.49	1.28	1.11111	0.52	1.31000	0.66
152LS1 R10 G3	2.67	1889	271	0.24	155	360	12.9	31.3	2.69	0.41	12.1	3.11	2.06	0.58824	0.31	1.62000	0.88
152LS1 R9 G8	2.26	1944	268	0.06	180	303	17.8	34.7	3.76	0.52	11.7	2.85	0.65	0.06173	0.03	1.04000	0.35
152LS1 R2 G3	2.13	1968	235	L.O.D.	140	342	14.6	37.0	8.26	0.61	10.0	4.54	0.56	9.00901	5.00	0.26000	0.28
152LS1 R4 G8	2.25	1959	269	L.O.D.	189	350	16.5	32.7	3.19	0.59	12.0	3.52	3.31	3.70370	2.06	14.00000	15.00
152LS1 R3 G2	1.79	1856	262	L.O.D.	163	350	16.2	36.7	3.53	0.66	16.0	7.07	0.52	4.27350	2.50	3.80000	3.30
152LS1 R1 G2	1.78	1742	266	L.O.D.	154	424	11.5	37.8	7.27	0.87	14.2	4.19	0.55	3.33333	2.00	0.73000	0.28
152LS1 R7 G10	2.25	1952	245	L.O.D.	183	313	15.2	34.1	4.18	0.57	7.9	1.59	0.43	0.05556	0.03	2.00000	1.30
152LS1 R6 G5	2.12	1873	260	L.O.D.	169	340	14.7	35.2	5.44	0.68	11.6	3.37	0.86	6.80272	4.60	0.17000	0.12
152LS1 R8 G8	2.81	2044	270	0.32	236	444	15.8	40.9	3.79	0.93	17.3	4.47	3.71	2.43902	1.67	4.50000	5.80

Table A5 – I: (Continued)

Sample Grain #	Sc ppm	V ppm	Cr ppm	Y ppm	Zr ppm	Nb ppm	Mo ppm	Sn ppm	Sb ppm	Hf ppm	Ta ppm	W ppm	U ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
152LS1 R9 G6	2.22	2000	275	L.O.D.	160	317	15.7	32.2	2.77	0.64	9.4	1.20	1.14	0.05556	0.04	1.49000	0.65
152LS1 R2 G5	2.29	1889	262	L.O.D.	153	319	14.5	29.8	4.76	0.85	10.0	3.10	0.44	0.43478	0.34	3.90000	4.70
152LS1 R9 G5	2.38	2058	243	L.O.D.	174	365	14.7	34.6	5.47	0.74	8.8	1.75	0.40	0.02778	0.02	1.64000	0.88
152LS1 R10 G10	3.06	1837	223	L.O.D.	136	279	11.2	35.4	7.14	1.10	10.0	6.07	0.23	26.31579	22.00	-0.04300	1.07
152LS1 R1 G7	2.34	1878	243	0.07	139	387	14.9	35.2	7.82	0.76	16.1	5.77	0.51	5.49451	5.30	0.57000	0.44
152LS1 R4 G3	2.04	1680	199	L.O.D.	196	368	13.6	30.8	4.10	1.80	13.1	3.60	0.81	7.63359	7.50	0.57000	0.89
152LS1 R7 G6	2.13	2003	254	L.O.D.	140	358	15.3	34.6	2.13	0.46	9.5	1.60	3.56	1.00000	1.00	0.59000	0.35
152LS1 R10 G9	2.46	1857	125	0.17	244	469	7.2	25.1	9.87	2.00	23.8	8.04	0.39	0.58824	0.62	3.60000	3.90
152LS1 R5 G6	2.40	1801	232	L.O.D.	140	322	15.0	31.0	1.68	0.43	9.2	2.05	2.55	1.81818	2.15	5.70000	6.40
152LS1 R9 G4	2.02	1929	277	L.O.D.	170	394	13.4	35.9	5.94	1.20	12.1	6.73	0.41	0.43478	0.53	15.50000	9.80
152LS1 R3 G7	3.05	1883	258	L.O.D.	193	317	16.4	37.0	5.31	0.99	9.4	3.28	0.57	8.62069	12.00	0.32000	0.25
152LS1 R1 G8	2.79	1779	251	0.04	144	407	10.7	35.9	7.92	0.77	19.4	5.91	0.35	1.58730	2.50	1.08000	0.49
152LS1 R8 G6	2.23	1838	227	L.O.D.	178	378	17.5	39.5	5.95	0.81	13.4	3.97	0.57	6.06061	10.00	0.65000	0.57
152-LS1B 3_5	L.O.D.	L.O.D.	21.1	L.O.D.	224	379	10.2	38.8	9.54	L.O.D.	23.6	7.12	0.36	5.55556	9.30	0.27000	0.59
152-LS1B 4_5	L.O.D.	L.O.D.	191	L.O.D.	168	329	10.9	31.3	5.56	L.O.D.	11.4	2.98	0.65	4.76191	8.00	1.00000	1.00
152LS1 R3 G5	4.14	1874	282	L.O.D.	150	441	13.1	34.3	7.47	0.95	23.5	6.40	0.27	10.63830	20.00	0.02600	1.50
152LS1 R1 G10	2.19	1944	227	L.O.D.	134	402	12.7	38.1	7.75	0.91	14.8	3.57	0.37	10.10101	19.00	-0.16000	0.87
152LS1 R7 G5	2.26	1811	244	L.O.D.	187	328	16.3	35.5	2.51	0.67	11.8	1.23	1.75	1.13636	2.40	0.52000	0.16
152LS1 R4 G4	1.52	2080	156	L.O.D.	148	325	12.6	27.0	5.30	1.10	10.3	4.90	0.49	5.84795	17.00	0.07000	0.42
152-LS1B 4_4	L.O.D.	L.O.D.	225	L.O.D.	226	361	10.2	37.8	7.81	L.O.D.	20.0	6.64	0.59	0.92593	3.10	0.64000	0.32
152LS1 R5 G9	2.12	1823	241	L.O.D.	129	337	14.8	32.3	2.36	0.41	10.0	2.01	1.60	0.57803	4.20	0.56000	0.13
152LS1 R3 G9	2.54	1877	265	0.17	186	373	13.1	34.1	3.54	0.70	6.4	2.16	1.03	0.05263	3.50	0.64000	0.16

Table A5 – I: (Continued)

230LS1													
Sample Grain #	Sc ppm	V ppm	Cr ppm	Y ppm	Zr ppm	Nb ppm	Mo ppm	Sn ppm	Sb ppm	Hf ppm	Ta ppm	W ppm	U ppm
230LS1 G1P1	20.5	1035	343	14.5	112	512	5.25	14.40	0.40	6.52	60.6	6.53	0.04
230LS1 G1P10	3.24	1310	467	0.05	238	393	9.47	22.20	0.86	11.7	16.4	6.64	L.O.D.
230LS1 G1P11	3.50	1367	486	L.O.D.	244	412	9.62	23.70	0.92	11.5	24.2	5.59	0.00
230LS1 G1P12	3.56	1369	502	L.O.D.	232	412	9.32	24.00	1.14	11.3	25.7	6.29	0.02
230LS1 G1P13	3.49	1348	502	L.O.D.	231	405	8.76	24.80	1.31	10.3	23.1	6.21	0.02
230LS1 G1P2	3.58	1422	556	0.19	255	513	13.9	27.60	1.24	11.5	25.1	7.05	0.01
230LS1 G1P3	3.70	1394	536	0.07	221	430	10.1	24.30	1.03	10.6	22.7	5.63	0.01
230LS1 G1P4	3.69	1417	539	0.29	213	395	9.50	28.00	1.16	10.2	21.4	6.50	0.02
230LS1 G1P5	3.57	1368	521	0.05	238	397	10.0	24.50	1.26	10.7	18.3	5.54	0.03
230LS1 G1P6	3.90	1368	518	0.13	227	406	9.15	25.30	1.09	10.5	21.9	6.99	0.01
230LS1 G1P7	3.88	1416	509	0.32	229	426	8.79	24.40	1.14	10.4	28.2	7.13	0.03
230LS1 G1P8	3.98	1378	499	L.O.D.	240	403	8.52	23.55	1.00	12.5	20.0	6.92	0.01
230LS1 G1P9	3.58	1337	491	L.O.D.	245	411	8.00	21.80	0.85	10.9	21.9	6.36	L.O.D.
230LS1 G2P1	3.65	1271	533	0.16	255	478	11.0	27.80	1.32	9.40	44.6	7.99	0.01
230LS1 G2P10	3.83	1239	518	L.O.D.	279	411	10.4	24.90	0.85	11.9	29.2	7.20	L.O.D.
230LS1 G2P11	3.93	1254	490	L.O.D.	278	407	9.87	25.30	1.02	11.4	26.6	6.81	0.01
230LS1 G2P12	4.13	1306	514	0.05	246	453	10.7	23.50	1.03	10.6	23.5	7.30	L.O.D.
230LS1 G2P13	3.97	1306	526	L.O.D.	284	463	10.3	26.00	0.87	12.2	39.0	7.17	0.01
230LS1 G2P14	3.49	1281	522	L.O.D.	244	390	11.6	27.50	1.02	11.8	27.8	5.92	L.O.D.
230LS1 G2P15	3.23	1265	501	L.O.D.	267	388	12.2	26.70	0.98	13.3	24.8	6.06	L.O.D.
230LS1 G2P2	3.67	1305	552	0.05	272	502	11.6	28.80	1.26	9.78	38.6	8.55	0.01
230LS1 G2P3	4.13	1331	540	L.O.D.	283	472	10.7	27.80	1.13	11.4	35.5	7.10	L.O.D.
230LS1 G2P4	3.69	1293	527	L.O.D.	287	476	11.4	25.90	0.97	12.7	45.4	7.64	L.O.D.
230LS1 G2P5	3.52	1277	522	L.O.D.	336	458	11.4	25.90	0.77	13.6	32.3	7.36	0.02
230LS1 G2P6	3.99	1263	503	L.O.D.	305	441	9.38	25.20	0.89	12.8	32.3	7.43	L.O.D.
230LS1 G2P7	4.01	1276	522	L.O.D.	307	436	9.65	26.20	0.86	13.2	27.2	7.53	0.01
230LS1 G2P8	4.72	1295	534	0.15	321	449	8.99	25.30	0.93	13.4	33.3	7.79	0.02
230LS1 G2P9	4.77	1322	536	L.O.D.	272	431	11.7	25.80	0.85	11.2	35.4	9.24	0.01
230LS1 G3P10	3.49	1282	490	L.O.D.	298	423	11.9	25.00	0.84	13.9	30.9	5.99	L.O.D.
230LS1 G3P11	3.91	1320	498	L.O.D.	319	442	13.3	27.70	0.71	13.4	40.0	6.77	L.O.D.
230LS1 G3P12	4.38	1260	482	L.O.D.	321	428	12.5	26.50	0.74	15.3	32.2	7.34	L.O.D.
230LS1 G3P13	5.24	1231	458	0.05	283	397	11.0	23.10	0.84	12.3	25.7	6.60	L.O.D.
230LS1 G3P4	3.10	1295	503	0.04	288	432	12.3	26.40	0.69	14.2	29.3	5.88	0.01
230LS1 G3P5	3.73	1310	520	L.O.D.	313	432	13.4	27.70	0.71	13.9	26.7	5.89	L.O.D.
230LS1 G3P6	5.04	1322	518	L.O.D.	282	435	13.8	28.40	0.87	13.0	29.1	6.33	L.O.D.
230LS1 G3P7	6.05	1251	479	0.12	301	375	11.3	27.80	0.97	12.6	10.5	5.20	0.02
230LS1 G3P8	3.57	1274	490	0.04	243	456	10.5	26.30	1.08	11.3	27.6	6.31	0.01
230LS1 G3P9	3.67	1270	486	0.05	287	411	11.6	26.80	0.74	14.5	27.0	6.22	L.O.D.
230LS1 G4P1	2.55	1115	480	L.O.D.	203	273	7.89	17.30	0.82	9.33	20.2	6.33	L.O.D.
230LS1 G4P2	4.78	1017	461	L.O.D.	244	410	6.69	22.90	1.06	12.5	32.2	7.19	L.O.D.
230LS1 G4P3	2.75	1148	473	L.O.D.	237	390	7.85	21.30	0.95	11.0	27.1	6.97	L.O.D.
230LS1 G4P4	3.34	1143	508	L.O.D.	237	411	7.89	22.92	1.06	11.2	30.3	6.85	L.O.D.
230LS1 G4P5	2.86	1117	506	0.04	216	486	7.51	20.84	1.05	10.9	26.3	6.55	L.O.D.
230LS1 G5P1	5.26	1246	479	0.27	253	373	8.81	21.10	0.98	11.2	27.0	6.97	L.O.D.
230LS1 G5P2	4.88	1249	494	L.O.D.	260	412	9.95	26.10	1.11	12.7	21.8	6.29	0.01
230LS1 G5P3	4.76	1270	491	L.O.D.	256	414	9.49	25.30	0.87	12.5	24.5	6.74	L.O.D.
230LS1 G5P4	3.76	1162	454	0.06	230	407	9.39	23.00	0.92	10.5	27.7	5.97	0.02
230LS1 G5P5	5.50	1284	501	0.11	245	463	10.8	25.00	1.10	10.9	35.2	6.78	0.04
230LS1 G5P6	5.29	1291	483	L.O.D.	328	420	10.2	26.30	0.78	13.7	26.1	6.75	0.16
230LS1 G5P7	5.18	1252	500	L.O.D.	373	391	10.8	25.00	0.55	14.5	24.9	5.89	0.23
230LS1 G5P8	4.51	1279	496	L.O.D.	377	434	12.6	29.00	0.86	14.4	27.0	6.87	0.26

Table A5 – II: Titanite trace elements and U-Pb analysis.

93LS1																		
	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
93LS1 R7G5	2.77	14.8	3.33	25.5	14.9	6.05	20.2	3.30	22.8	4.42	12.6	1.71	11.3	1.21	0.38168	0.07	0.88000	0.04
93LS1 R1G8	11.8	74.6	17.6	113	40.1	11.6	35.8	4.31	25.4	4.84	13.2	1.69	9.25	1.12	0.29674	0.02	0.85700	0.02
93LS1 R2G3	9.20	62.3	15.2	101	36.4	12.9	33.1	4.19	25.3	4.69	12.4	1.47	8.50	0.93	0.19531	0.02	0.86100	0.02
93LS1 R4G6	8.62	58.5	16.2	120	53.6	15.3	45.8	5.48	30.8	5.68	14.1	1.32	6.25	0.59	0.23810	0.02	0.85300	0.02
93LS1 R7G2	10.2	69.9	18.0	122	48.8	18.6	45.3	5.67	29.9	5.28	13.5	1.60	8.24	0.87	0.28090	0.02	0.87100	0.02
93LS1 R5G1	9.56	70.0	18.6	129	53.3	19.7	52.5	5.73	31.9	5.67	14.0	1.61	8.61	1.03	0.22573	0.02	0.87700	0.03
93LS1 R2G6	6.43	45.6	13.0	101	55.6	20.5	56.7	7.53	38.9	5.41	10.6	0.86	3.77	0.33	0.20121	0.02	0.87300	0.02
93LS1 R9G7	4.32	27.1	7.48	58.8	44.1	20.8	59.5	9.10	55.3	9.97	29.1	3.90	25.0	2.69	0.68027	0.05	0.83900	0.04
93LS1 R6G3	11.4	77.5	20.5	138	57.6	21.8	59.4	7.09	38.5	7.08	18.2	2.11	11.1	1.33	0.40323	0.02	0.86600	0.03
93LS1 R3G1	16.4	110.2	27.6	185	68.5	23.1	63.3	7.56	43.2	7.87	21.2	2.56	14.8	1.67	0.37736	0.02	0.86000	0.02
93LS1 R4G2	9.29	69.4	19.7	145	68.8	24.7	68.5	7.88	43.6	6.99	15.8	1.61	7.75	0.78	0.35714	0.03	0.87400	0.02
93LS1 R1G9	28.5	174.1	40.2	241	77.3	26.6	65.7	8.03	48.9	9.31	27.2	3.38	20.0	2.51	0.79428	0.04	0.85500	0.02
93LS1 R9G2	29.5	173.7	39.3	245	79.9	27.5	64.8	7.67	44.6	8.64	24.4	3.16	18.3	2.16	0.86281	0.03	0.82200	0.02
93LS1 R7G4	11.8	82.6	23.3	169	76.7	28.4	74.8	9.27	49.9	8.66	20.9	2.36	12.5	1.33	0.40650	0.04	0.86800	0.03
93LS1 R7G1	17.4	117.4	30.8	196	78.2	29.5	72.3	8.60	45.3	8.18	21.1	2.49	12.5	1.44	0.48780	0.03	0.85300	0.02
93LS1 R2G5	16.4	114.1	31.7	225	97.6	35.9	94.4	11.9	68.4	12.4	32.0	3.89	22.4	2.44	0.53619	0.03	0.86400	0.02
93LS1 R8G6	20.4	140.1	37.6	261	110	40.2	101	12.7	68.9	11.9	30.7	3.60	19.0	2.12	0.72993	0.07	0.82300	0.02
93LS1 R6G4	13.7	105.3	30.6	224	108	43.5	104	11.1	51.8	7.60	15.8	1.66	8.30	0.75	0.79428	0.05	0.83700	0.03
93LS1 R3G3	17.7	129.1	36.1	259	120	44.7	115	13.8	73.2	12.7	30.6	3.52	17.9	1.83	0.72254	0.04	0.84300	0.02
93LS1 R3G5	10.1	62.7	16.6	122	77.5	45.7	104	12.1	48.1	5.18	10.7	1.40	13.0	2.40	1.73010	0.42	0.76700	0.03
93LS1 R4G3 rim	11.2	85.7	26.9	211	120	46.9	124	13.8	63.5	9.04	19.1	2.02	8.96	0.86	0.56180	0.04	0.85000	0.02
93LS1 R6G9 rim	12.8	96.0	29.0	239	132	50.3	137	16.3	81.9	12.6	29.4	2.75	13.1	1.13	0.62893	0.04	0.83500	0.02
93LS1 R9G8	23.1	157.0	42.8	309	145	52.8	136	16.9	95.5	16.7	40.1	4.52	24.7	2.61	0.97371	0.03	0.83400	0.02
93LS1 R9G4	18.5	129.9	37.3	287	144	52.8	144	16.6	85.9	13.6	32.8	3.66	18.9	1.93	0.69881	0.04	0.84400	0.02
93LS1 R8G4	82.1	352.0	68.6	374	131	68.6	148	16.4	63.6	6.88	10.3	0.93	3.62	0.30	3.57782	0.12	0.65700	0.02
93LS1 R5G8	135	596.0	115	644	211	88.5	200	20.1	75.9	8.14	12.8	1.04	5.03	0.43	3.36700	0.16	0.66900	0.02
93LS1 R7G6	20.0	121.2	33.3	228	117	71.8	157	17.3	58.8	5.98	8.70	0.71	2.91	0.32	3.41297	0.19	0.68400	0.04
93LS1 R6G1	76.2	390.0	87.3	525	200	95.2	205	20.1	64.9	6.46	10.1	0.80	3.75	0.44	3.96825	0.17	0.63900	0.02
93LS1 R5G2	78.0	327.0	61.6	353	128	60.9	141	14.9	58.8	6.17	9.71	0.83	3.72	0.35	2.86533	0.23	0.69700	0.04

Table A5 – II: (Continued)

	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
93LS1 R5G6	96.9	447.0	87.9	520	184	89.0	195	19.3	69.2	6.84	10.3	0.84	3.68	0.29	3.54610	0.12	0.65600	0.03
93LS1 R3G6	46.8	273.0	66.4	461	217	92.2	207	18.4	61.9	5.94	8.74	0.76	3.00	0.27	2.89855	0.15	0.72400	0.02
93LS1 R3G10	44.2	260.0	64.0	434	204	99.5	210	19.6	67.0	6.27	8.89	0.67	2.97	0.22	2.99401	0.14	0.71100	0.03
93LS1 R6G9 core	33.4	182.8	42.2	288	131	63.1	157	16.0	56.8	5.98	9.27	0.80	2.99	0.28	2.11417	0.16	0.75700	0.03
93LS1 R6G7	69.7	367.0	83.7	529	217	98.4	213	18.8	63.2	6.20	9.18	0.75	2.79	0.20	3.80228	0.16	0.65500	0.03
93LS1 R3G7	92.2	424.0	83.1	484	168	86.6	183	18.1	67.0	6.45	10.3	0.90	3.89	0.34	3.55872	0.16	0.66400	0.02
93LS1 R4G3 core	132	607.0	118	687	246	99.1	219	20.0	70.0	7.27	11.2	0.86	3.34	0.30	3.81825	0.14	0.64200	0.02
93LS1 R7G3	114	500.0	95.1	506	161	62.3	153	15.5	58.7	6.34	11.4	1.02	4.16	0.39	3.01205	0.22	0.70700	0.04
93LS1 R9G1	25.5	153.6	40.6	304	182	105.9	233	22.4	73.9	6.22	8.65	0.69	2.59	0.41	3.26797	0.22	0.67700	0.02
93LS1 R4G1	75.7	405.0	93.4	598	241	99.3	224	20.0	67.5	6.83	10.2	0.89	3.39	0.31	3.44828	0.15	0.69200	0.02
93LS1 R4G4 rim	37.0	195.0	45.3	318	162	73.9	175	18.1	69.6	7.18	11.9	0.95	3.85	0.29	0.97087	0.28	0.82400	0.03
93LS1 R1G10	87.5	416.0	82.6	457	137	62.2	136	14.1	56.8	6.32	10.4	0.88	3.86	0.31	3.59712	0.14	0.65900	0.02
93LS1 R2G4	75.5	409.0	92.5	611	252	104	235	20.6	68.7	6.53	10.4	0.85	3.20	0.28	3.61011	0.17	0.67300	0.03
93LS1 R1G3 core	192	774.0	131	676	191	75.6	165	16.8	67.3	8.02	14.2	1.24	5.71	0.50	2.19298	0.09	0.75000	0.01
93LS1 R6G5	40.0	215.0	54.0	348	153	84.9	181	18.5	64.9	6.17	8.99	0.74	2.68	0.26	4.16667	0.36	0.61000	0.04
93LS1 R4G7 core	84.2	438.0	98.3	612	237	103	223	20.0	67.4	6.61	9.67	0.81	3.33	0.25	3.89712	0.14	0.63000	0.03
93LS1 R8G5	31.3	185.0	49.1	356	183	102	206	19.6	61.4	5.81	8.12	0.64	2.56	0.20	3.80228	0.20	0.64100	0.03
93LS1 R1G3 rim	102	492.0	100	588	206	81.9	184	17.9	69.4	7.66	12.5	1.10	4.86	0.36	2.78552	0.16	0.71200	0.02
93LS1 R4G5	21.8	130.0	33.3	229	130	67.5	164	16.1	55.9	5.40	8.22	0.56	2.74	0.24	1.77620	0.18	0.77500	0.03
93LS1 R1G6	13.9	96.0	27.2	222	155	88.0	204	23.1	79.3	6.79	8.00	0.53	2.71	0.15	2.33645	0.26	0.71700	0.05
93LS1 R2G10	71.0	357.0	76.3	493	218	115	232	22.2	72.5	6.68	9.00	0.71	2.85	0.18	4.50451	0.25	0.60700	0.03
93LS1 R4G9	65.5	363.0	87.2	600	255	113	247	22.1	71.9	6.59	9.87	0.76	2.91	0.24	3.76223	0.13	0.65400	0.02
93LS1 R8G2	83.2	538.0	144	991	448	166	382	34.3	114.1	11.2	15.9	1.25	5.06	0.33	2.26244	0.18	0.73100	0.03
93LS1 R4G4 core	44.7	247.0	56.5	374	151	77.0	168	16.9	61.6	6.39	9.74	0.72	3.34	0.31	3.63636	0.15	0.67400	0.03
93LS1 R7G7	61.4	316.0	75.2	472	227	117	241	23.3	72.0	6.67	8.80	0.66	2.66	0.27	4.46429	0.41	0.62300	0.04
93LS1 R1G4	58.7	291.0	62.4	393	172	97.3	217	22.8	84.2	7.90	10.03	0.67	2.85	0.20	4.04858	0.20	0.62900	0.03
93LS1 R6G8	30.7	182.0	45.7	312	157	87.4	195	18.9	65.4	5.80	8.50	0.77	4.00	0.40	3.50877	0.27	0.69000	0.05
93LS1 R5G7	135	666.0	142	877	335	121	276	24.9	83.9	9.07	13.8	1.10	4.78	0.38	2.80112	0.16	0.69300	0.02
93LS1 R5G3	46.3	267.0	63.4	418	185	85.9	193	18.0	62.6	6.42	9.40	0.71	2.84	0.28	3.28947	0.27	0.69000	0.03
93LS1 R3G4	47.7	288.0	74.1	530	254	111	233	20.4	63.5	5.89	9.21	0.74	3.10	0.26	3.59712	0.21	0.64900	0.03

Table A5 – II: (Continued)

	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
93LS1 R9G5	89.6	420.0	85.4	491	185	86.1	194	19.0	73.4	7.69	12.8	1.05	4.89	0.45	3.00300	0.29	0.69700	0.04
93LS1 R6G6	44.6	269.0	74.7	499	237	94.9	217	21.8	85.5	8.89	13.5	1.16	4.40	0.49	1.22699	0.10	0.77900	0.05
93LS1 R9G11 rim	53.1	276.0	63.5	399	156	83.0	176	17.9	66.9	6.82	10.2	0.92	4.28	0.37	4.00000	0.21	0.65100	0.03
93LS1 R2G1 core	98.1	479.0	101	617	236	115	225	20.6	68.4	6.32	9.23	0.78	3.18	0.30	4.57876	0.16	0.61500	0.02
93LS1 R8G10	21.8	128.0	30.9	221	107	61.0	139	16.1	60.2	6.01	8.43	0.60	2.63	0.19	3.44828	0.52	0.70700	0.09
93LS1 R8G8	20.4	124.2	33.9	262	169	106	231	25.0	82.9	7.29	9.51	0.81	3.80	0.54	3.96825	0.14	0.63500	0.02
93LS1 R7G9	88.3	447.0	103	658	261	126	257	23.4	73.7	6.87	9.18	0.64	3.08	0.24	4.48431	0.27	0.61500	0.03
93LS1 R3G8	55.5	299.0	68.3	467	209	105	224	21.1	69.1	6.48	9.30	0.71	3.13	0.31	3.84172	0.11	0.66400	0.03
93LS1 R9 G10	20.9	124.0	33.5	262	174	106	240	23.8	74.8	5.80	7.74	0.50	1.89	0.15	3.31126	0.64	0.69600	0.05
93LS1 R2G2	78.7	394.4	81.5	477	166	68.6	166	15.8	60.8	6.80	11.7	0.99	4.04	0.37	3.58423	0.14	0.67300	0.02
93LS1 R2G8	63.8	357.0	84.3	551	235	103	217	19.1	64.0	5.98	9.29	0.69	3.20	0.29	3.46021	0.19	0.68000	0.02
93LS1 R3G2	97.0	463.0	92.0	538	192	88.4	197	19.3	69.1	7.21	11.4	0.92	3.84	0.33	3.80228	0.17	0.66100	0.02
93LS1 R5G9	25.6	164.0	46.3	356	207	97.0	229	21.2	67.7	6.17	8.97	0.70	2.66	0.26	2.05339	0.17	0.73400	0.03
93LS1 R7G10	88.0	425.0	94.1	574	217	98.4	200	19.1	64.6	6.19	9.32	0.77	3.35	0.22	4.21941	0.22	0.65600	0.04
93LS1 R4G8	95.2	433.0	81.7	453	133	58.7	140	14.2	57.3	6.37	11.0	0.90	4.41	0.37	3.62319	0.17	0.65000	0.03
93LS1 R8G10	41.8	254.0	63.9	457	223	100	230	21.5	68.2	6.14	8.75	0.75	3.15	0.25	3.71747	0.16	0.68100	0.04
93LS1 R2G1 rim	13.0	110.2	37.6	320	210	89.0	216	20.9	73.1	7.15	10.7	0.90	2.99	0.28	1.02250	0.04	0.82900	0.02
93LS1 R4G10	219	648.0	100	506	136	58.6	133	14.4	59.3	7.07	12.9	1.16	4.96	0.48	3.35571	0.18	0.67500	0.02
93LS1 R2G9	17.6	111.7	31.5	264	188	130	277	29.0	92.4	7.19	9.17	0.58	2.17	0.21	4.06504	0.20	0.60000	0.02
93LS1 R6G10	32.2	193.7	52.3	386	208	108	234	22.2	68.9	6.19	8.54	0.65	2.57	0.19	3.71747	0.17	0.64900	0.02
93LS1 R4G7 rim	127	581.0	116	686	239	103	218	20.4	73.8	7.25	11.4	0.97	3.75	0.31	3.61011	0.26	0.65500	0.03
93LS1 R8G3	42.8	243.2	58.4	385	164	83.0	189	20.6	71.7	6.93	10.1	0.74	2.91	0.21	4.42478	0.24	0.61200	0.03
93LS1 R1G7	53.0	288.0	69.0	466	230	120	239	23.2	73.4	6.50	8.85	0.72	3.41	0.29	2.96736	0.10	0.70100	0.03
93LS1 R6G6 core	92.0	435.0	88.4	505	184	87.4	187	18.9	68.1	6.78	11.0	0.84	3.38	0.34	3.96825	0.22	0.64500	0.03
93LS1 R2G7	51.5	260.0	58.3	379	176	95.7	213	22.1	79.1	7.20	10.3	0.70	2.78	0.24	3.00300	0.12	0.72800	0.02
93LS1 R1G5	96.3	484.0	106	678	284	128	251	21.9	72.2	6.55	10.4	0.76	3.79	0.30	4.31406	0.15	0.61500	0.02
93LS1 R8G2 core	42.4	229.0	56.1	375	168	94.8	195	19.9	65.6	6.15	9.16	0.70	2.81	0.25	4.00000	0.18	0.65600	0.03
93LS1 R1G2	108	656.0	170	1172	569	209	459	40.3	138	12.6	18.1	1.41	5.60	0.55	2.84900	0.18	0.70900	0.03

Table A5 – III: Apatite trace elements and U-Pb analysis.

183LS1																		
Grain #	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm pp	Yb ppr	Lu ppr	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
R2G2	1.03	2.54	5.02	12.7	24.5	9.46	51.8	41.9	44.5	51.6	58.5	47.1	54.2	61.7	1.12360	0.18	0.75700	0.06
R7G8	1.10	1.57	2.29	3.01	5.85	3.82	15.3	16.5	21.5	27.5	34.3	31.6	34.7	50.6	2.59067	0.29	0.70200	0.05
R2G6	1.33	2.88	4.37	12.2	25.1	11.8	46.9	42.4	45.0	46.2	56.2	50.0	51.4	60.9	2.34742	0.30	0.67600	0.04
R7G6	2.51	3.90	7.30	14.7	30.3	15.4	64.5	51.8	59.0	59.0	66.4	53.7	56.8	66.7	3.00300	0.34	0.64800	0.05
R1G7	3.79	12.4	33.1	77.1	137	43.8	133	65.8	48.0	39.9	39.5	28.7	28.6	36.6	2.89017	0.33	0.67100	0.04
R2G10	4.81	11.7	25.9	58.1	95.9	32.3	130	79.3	70.3	65.5	70.5	60.3	56.1	64.1	5.66893	0.58	0.49600	0.04
R5G9	9.03	12.3	18.0	30.3	38.1	22.9	61.0	44.4	42.1	43.2	43.0	37.6	33.2	39.5	2.20751	0.36	0.68000	0.06
R7G4	10.3	15.0	25.9	43.8	66.6	29.3	78.8	41.6	41.0	38.1	42.5	37.8	37.7	46.9	2.27273	0.26	0.67800	0.04
R1G3	11.8	20.7	38.5	80.0	119	41.8	140	79.1	63.5	57.0	56.8	45.6	48.4	60.9	3.58423	0.27	0.63700	0.04
R6G1	12.4	23.0	43.2	86.9	131	46.4	150	70.8	53.9	46.9	48.0	38.5	39.1	46.1	4.40529	0.49	0.60700	0.04
R3G5 RIM	12.5	28.7	54.7	101	149	60.0	141	67.5	56.7	47.8	47.7	34.3	33.5	43.5	3.77359	0.34	0.58900	0.04
R2G1	16.2	37.8	74.4	149	203	80.9	190	79.9	55.2	40.6	33.5	26.0	25.7	30.5	6.06061	0.62	0.49500	0.03
R3G4 RIM	23.1	35.3	57.4	92.2	105	28.0	91.0	46.8	33.7	28.6	26.6	22.7	22.0	29.8	4.38597	0.60	0.56100	0.08
R8G9	26.7	48.4	83.7	155	201	115	203	98.1	66.1	50.2	42.5	39.0	35.1	35.9	5.10204	0.60	0.56500	0.06
R8G3	30.1	43.3	60.6	101	128	51.1	138	73.8	56.0	45.9	41.0	35.0	32.0	38.7	4.20168	0.44	0.56900	0.06
R1G4 RIM	33.3	46.9	71.7	116	143	81.1	141	78.5	66.3	59.5	63.6	59.6	57.7	69.5	1.98413	0.22	0.71500	0.04
R7G2	33.6	59.8	101	182	232	86.1	220	101	70.9	61.2	53.3	40.8	40.5	47.3	3.66300	0.40	0.65600	0.04
R5G10 RIM	47.5	73.3	114	193	230	94.3	198	97.8	70.6	57.7	53.4	43.3	44.1	52.1	3.95257	0.36	0.65500	0.04
R2G7	51.2	60.8	80.1	132	172	88.8	157	77.7	57.3	42.6	35.2	29.7	26.5	32.9	3.17460	0.44	0.63800	0.04
R1G6	63.6	65.5	83.3	116	127	68.2	130	73.8	53.6	47.5	42.8	31.9	32.6	37.3	3.74532	0.36	0.62600	0.04
R3G3	64.3	95.7	146	236	285	138	232	102	61.4	41.0	34.7	23.9	21.6	24.3	4.48431	0.50	0.59700	0.05
R1G4 CORE	69.0	111	185	297	347	178	274	120	77.0	54.5	46.4	33.4	30.6	36.6	3.15457	0.36	0.71700	0.04
R8G10 RIM	72.0	97.5	142	216	257	125	222	100	66.4	46.2	36.1	25.0	24.0	26.6	4.03226	0.28	0.58000	0.03
R7G3 RIM	72.4	99.5	141	221	263	143	192	99	65.5	48.2	44.2	31.8	34.3	37.9	4.04858	0.49	0.66200	0.06
R7G5	90.8	118	166	249	264	164	238	108	67.2	45.0	38.8	25.5	23.9	26.4	6.65779	0.66	0.46100	0.04
R1G9 RIM	91.2	143	217	341	376	208	266	114	69.4	44.6	35.2	23.6	19.6	23.4	4.69484	0.33	0.52800	0.04
R4G1	94.6	104	126	184	191	93.9	182	91.2	61.3	44.2	39.7	32.8	26.7	31.3	5.07614	0.57	0.61100	0.07
R10G9	98.3	77.8	80	100	92.5	58.6	116	75.2	66.0	58.5	56.1	40.7	40.7	38.6	1.73913	0.21	0.74900	0.04

Table A5 – III: (Continued)

Grain #	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm pp	Yb pp	Lu pp	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
R3G2	101	171	279	440	525	281	369	169	111	71.8	53.2	34.0	31.6	32.9	3.58423	0.41	0.62600	0.04
R5G2 RIM	115	105	123	172	178	102	162	82.9	62.2	46.8	40.4	30.2	27.3	30.5	2.54453	0.28	0.70800	0.04
R9G3 RIM	141	115	126	168	164	88.0	162	84.0	65.8	56.1	51.8	44.0	40.1	40.2	3.47222	0.25	0.64600	0.03
R4G10	142	191	264	387	419	244	329	145	91.1	63.8	52.7	37.6	33.2	33.9	4.56621	0.48	0.67200	0.06
R8G5	153	128	140	187	182	105	175	87.9	63.5	53.1	49.7	34.7	35.4	35.8	3.36700	0.41	0.63100	0.06
R4G6 RIM	161	125	125	152	137	80.4	142	74.9	61.9	49.8	50.6	40.5	37.4	41.6	2.15983	0.27	0.77300	0.04
R4G8 CORE	163	253	376	561	638	346	396	167	98.1	57.4	35.7	20.8	14.6	16.7	4.40529	0.35	0.64900	0.04
R5G5	182	184	230	325	315	204	276	123	85.7	56.8	50.0	39.3	32.9	37.4	2.40964	0.37	0.73500	0.04
R5G3	190	175	208	281	283	176	267	129	85.7	65.1	56.9	45.8	43.3	46.5	4.29185	0.44	0.61800	0.03
R2G4	211	224	281	378	385	227	321	140	88.2	59.4	39.6	30.6	23.4	23.8	5.15464	0.58	0.54100	0.03
R1G2 CORE	217	272	364	524	573	322	377	159	104	69.1	51.5	33.1	28.6	28.7	3.37838	0.23	0.64300	0.03
R2G5	219	315	439	631	704	364	453	187	113	68.3	46.5	27.6	21.7	23.4	2.65252	0.17	0.71100	0.03
R2G8	223	281	369	534	559	336	377	161	100	62.8	42.8	26.2	23.2	25.4	4.25532	0.33	0.60400	0.03
R3G4 CORE	227	324	466	652	704	384	460	190	106	63.8	41.0	24.3	16.4	18.4	5.46448	0.60	0.49700	0.03
R5G10 CORE	231	266	350	501	522	296	360	153	99	65.1	46.9	30.8	31.1	32.8	4.06504	0.26	0.63400	0.03
R1G8	235	279	376	526	569	325	407	179	105	66.4	46.6	28.3	27.8	26.2	3.58423	0.35	0.62200	0.03
R8G4	236	213	230	293	273	176	238	126	89.7	65.5	52.2	40.0	32.3	35.4	4.44444	0.49	0.57100	0.03
R9G4	244	205	223	271	262	163	224	127	93.9	75.7	64.4	45.1	38.2	33.8	0.76394	0.08	0.78700	0.02
R10G6	245	211	242	314	311	175	258	123	85.3	57.9	49.7	37.6	32.2	30.3	2.34192	0.29	0.68300	0.05
R10G7	255	259	322	453	467	278	388	177	115	78.1	58.8	37.8	30.3	32.2	3.59712	0.25	0.62500	0.03
R9G6	256	293	373	508	522	313	375	165	97.7	59.4	46.0	28.2	25.5	21.3	1.82815	0.22	0.69500	0.04
R1G9 CORE	261	293	364	493	494	286	332	148	90.4	60.3	42.9	25.2	24.9	22.3	3.93701	0.31	0.62500	0.03
R3G10	263	356	484	683	707	379	438	186	109	68.9	49.1	31.0	26.0	27.1	1.89036	0.13	0.73900	0.03
R3G8	282	220	241	301	271	165	228	116	73.8	55.2	44.3	32.7	29.2	34.2	1.74216	0.17	0.75300	0.04
R5G7	287	278	318	408	385	223	290	126	78.3	50.0	39.4	26.0	23.0	19.6	3.28947	0.34	0.66300	0.03
R4G2	315	358	450	601	629	404	407	177	103	62.4	42.8	26.2	18.1	16.8	1.55763	0.17	0.71700	0.03
R3G5 CORE	321	417	540	732	769	453	481	213	125	72.5	43.9	27.7	19.3	15.6	4.01606	0.37	0.65700	0.04
R8G1	331	238	224	271	196	127	196	96	71.4	55.4	48.8	35.3	32.7	34.2	1.77620	0.19	0.74100	0.03

Table A5 – III: (Continued)

Grain #	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm pp	Yb pp	Lu pp	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE
R1G5	333	450	633	831	889	525	546	217	131	72.1	44.3	28.0	19.1	15.8	3.75940	0.40	0.68000	0.12
R3G9	340	327	396	525	520	329	381	187	122	81.3	64.3	47.5	45.1	48.4	1.34771	0.11	0.76900	0.03
R7G3 CORE	347	410	521	694	661	394	448	195	118	71.8	49.3	34.3	28.4	28.8	4.84262	0.45	0.57000	0.03
R1G10	362	464	623	824	876	584	645	300	176	101	63.9	34.7	24.0	22.6	2.80899	0.32	0.68900	0.03
R4G4	364	469	611	791	789	482	475	205	114	70.3	46.1	26.5	17.3	18.2	2.24719	0.25	0.69800	0.03
R3G1	370	408	508	656	653	393	439	202	115	65.1	40.1	23.1	19.3	15.8	2.32558	0.23	0.71700	0.04
R4G7	372	365	452	592	554	355	415	179	113	61.3	36.9	21.9	16.5	15.1	3.03030	0.37	0.70400	0.03
R5G4	375	385	446	550	555	336	397	177	110	69.6	48.8	31.8	24.0	23.7	2.08768	0.31	0.72200	0.04
R6G6	404	287	280	333	287	178	254	122	84.7	60.3	47.3	38.5	34.6	34.0	1.31406	0.10	0.78500	0.03
R5G2 CORE	411	317	329	391	356	223	276	133	88.6	61.9	47.1	31.0	28.6	27.5	0.44843	0.06	0.83100	0.03
R9G2 CORE	413	362	398	514	494	295	403	182	112	69.1	49.9	34.6	25.5	26.4	1.93424	0.12	0.73600	0.02
R10G10	425	300	281	338	305	188	256	121	82.0	58.5	49.5	37.4	32.9	33.5	1.07411	0.07	0.79100	0.02
R6G5	426	401	443	550	517	318	381	167	103	68.2	46.6	33.5	26.3	22.8	0.48544	0.08	0.80300	0.03
R8G10 CORE	431	458	552	732	700	446	464	203	119	72.3	46.8	26.6	20.8	19.5	1.10742	0.07	0.80000	0.02
R4G6 CORE	439	303	302	336	298	179	259	120	77.0	52.9	43.9	28.4	27.0	23.3	0.69396	0.07	0.81200	0.02
R5G6	441	484	587	758	765	450	513	227	134	78.2	48.3	25.9	18.1	16.3	1.35870	0.14	0.75000	0.03
R7G10	447	385	421	519	502	315	368	167	113	77.0	58.4	38.4	32.0	32.8	0.66050	0.07	0.79800	0.02
R1G1	449	384	422	553	524	304	393	179	107	66.0	46.1	28.7	23.6	22.8	1.25000	0.09	0.76300	0.02
R6G2	475	401	416	502	442	286	326	147	90.6	62.9	49.3	35.9	33.7	33.3	0.63291	0.07	0.78800	0.02
R8G7	502	531	630	847	827	518	523	228	135	81.7	54.9	32.5	23.5	21.6	1.20627	0.13	0.79200	0.05
R9G5	503	537	654	827	816	511	508	222	139	86.9	58.7	35.7	24.2	25.8	0.80645	0.10	0.75600	0.02
R6G4	514	544	642	789	773	471	502	223	138	81.1	52.2	31.9	20.6	20.5	0.98814	0.10	0.77800	0.02
R4G5	527	589	709	931	912	562	549	235	139	86.9	60.5	32.1	25.1	23.6	0.54645	0.06	0.83500	0.02
R4G9	528	526	618	754	729	471	549	260	147	82.2	52.0	31.0	20.4	18.6	0.91158	0.09	0.77200	0.02
R10G4 CORE	533	381	360	418	359	220	299	143	90.7	59.2	42.9	28.7	23.3	19.3	0.65062	0.05	0.81500	0.01
R6G8	538	630	816	1026	970	618	556	250	145	86.7	54.2	32.1	25.8	21.7	0.78493	0.09	0.79400	0.03
R5G1	544	527	624	805	763	479	532	244	137	80.6	50.2	28.6	24.1	17.4	0.50000	0.05	0.80700	0.02
R10G2	574	642	772	970	940	585	570	245	146	84.0	51.6	31.6	19.9	15.8	0.64185	0.04	0.81100	0.02
R2G9	584	602	697	866	805	498	525	241	145	90.8	58.4	36.4	27.9	28.4	0.89606	0.07	0.77100	0.03
R10G8	623	584	644	811	746	454	565	244	148	86.2	53.6	31.8	24.5	21.5	0.79428	0.05	0.80700	0.02
R4G3	694	736	854	1068	1037	654	636	291	180	110	68.8	39.0	29.4	23.0	0.42194	0.03	0.83500	0.01

Table A5 – IV: Zircon trace elements and U-Pb analysis.

205LS1 LA-ICPMS data																							
Analysis #	Sample	rain #	Domain colour	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Th/U	²³⁸ U/ ²⁰⁶ Pb	Error 2SE	²⁰⁷ Pb/ ²⁰⁶ Pb	Error 2SE	
1	205LS1	G8	bright	<MDL	0.0185	<MDL	<MDL	<MDL	<MDL	<MDL	0.0211	0.767	1.01	22.49	17.16	391	151.5	0.0013	13.69863	0.4128354	0.056	0.0032	
2	205LS1	G83	bright	0.074	0.102	0.0186	0.097	0.233	0.235	5.57	3.84	84.7	49.7	390	143.3	2243	586	0.00592	13.67989	0.4865625	0.0738	0.0067	
3	205LS1	G6	bright	0.0332	0.116	0.0292	0.259	0.74	1.241	21.99	14.01	250.6	122.9	808	239.8	2776	520	0.01506	12.64223	0.3995646	0.1452	0.0093	
4	205LS1	G28	bright	0.053	0.168	0.0067	0.031	0.016	<MDL	0.157	0.104	2.31	1.84	18.56	7.74	132	42.1	0.0101	13.86963	0.3654964	0.0559	0.0023	
5	205LS1	G54	bright	0.46	1.52	0.24	1.49	1.74	1.13	16.8	6.64	81.6	31.3	208	74.4	1157	302.6	0.00714	13.92758	0.5431367	0.0973	0.01	
6	205LS1	G89	bright	0.98	10	1.43	12.6	5.43	3.19	8.8	1.35	14.4	8.11	112.2	76	1517	446	0.00383	13.67989	0.3368509	0.0652	0.0035	
7	205LS1	G56	bright	2.35	2.93	0.4	2.09	0.61	0.234	1.77	1.19	34.4	31.11	376.2	174.4	2625	587	0.00026	13.60544	0.3887269	0.0584	0.002	
8	205LS1	G26	bright	0.05	0.136	0.0222	0.093	0.053	0.06	0.55	0.365	10.67	12.5	197	98.7	1480	381	0.00172	13.947	0.4862971	0.0621	0.0027	
9	205LS1	G21	bright	0.0222	0.049	0.0059	0.099	0.031	0.035	0.427	0.426	14.6	15.2	195	103.6	1980	630	0.00015	13.56852	0.3313886	0.0634	0.0039	
10	205LS1	G44	bright	0.0114	0.076	0.0055	0.064	0.104	0.091	2.04	1.64	42.7	28.6	216	81	1130	246	0.00485	13.42282	0.4504302	0.0679	0.0045	
11	205LS1	G19	bright	0.096	0.165	0.034	0.2	0.082	0.061	0.29	0.19	4.66	2.33	18.1	6.1	94	23.5	0.0001	12.90323	0.5827263	0.0832	0.0043	
12	205LS1	G20	bright	0.178	1.38	0.284	2.76	1.73	0.67	3.28	0.781	12.28	8.06	71.3	30	489	126	0.00446	11.80638	0.4878668	0.1403	0.0066	
13	205LS1	G29	bright	0.46	3.4	0.42	2.77	0.81	0.36	2.3	1.02	20.8	16	143.2	61.4	1025	282	0.00037	14.72754	0.4338009	0.0745	0.0078	
14	205LS1	G30	bright	0.6	3.26	0.51	2.76	0.82	0.212	1.31	0.544	23.2	31.4	485	241.1	3720	991	0.00068	14.51379	0.4002351	0.0626	0.0023	
15	205LS1	G12	bright	0.58	5.1	0.33	1.83	0.64	0.253	2.94	2.01	52.1	36.1	349	144	2440	640	0.01351	14.16431	0.4012551	0.0808	0.0053	
16	205LS1	G31	bright	0.147	2.09	0.52	9.2	20.7	9.85	82.6	19.8	150	36	136	30.8	338	68.4	0.005	12.33046	0.4409164	0.0659	0.0033	
17	205LS1	G52	bright	0.256	0.992	0.111	0.69	0.344	0.087	0.6	0.25	6.78	5.66	65.3	35	668	192	0.00074	12.31527	0.4094979	0.0707	0.0046	
18	205LS1	G60	bright	0.0091	0.0191	<MDL	<MDL	<MDL	0.055	1.22	1.27	34.7	26.7	247	107.7	1980	565	0.00012	13.02083	0.406901	0.057	0.0028	
19	205LS1	G81	bright	<MDL	<MDL	<MDL	<MDL	0.088	0.115	1.77	1.066	20.2	9.49	66.8	20.3	257.5	64.4	0.00015	14.45087	0.3758896	0.0642	0.0033	
20	205LS1	G86	bright	<MDL	0.107	0.0232	0.549	3.25	2.26	29.4	11.07	156	62.9	357	111	1420	321	-0.00002	14.10437	0.4575466	0.0875	0.0085	
21	205LS1	G89	dark	0.67	5.8	0.82	7.7	3.9	1.88	12.4	5.69	120.6	77.2	595	192.1	2343	550	0.00383	14.30615	0.4093319	0.0587	0.002	
22	205LS1	G76	dark	<MDL	0.039	0.0088	0.081	0.046	0.026	0.163	0.118	3.4	2.43	25.82	13.61	279	73.3	0.00014	14.02525	0.3540735	0.0619	0.0023	
23	205LS1	G12	dark	15.75	46.6	7.21	41.9	18.8	12.91	33.2	9.86	129.9	61.4	444	139.6	1703	407	0.01351	13.1406	0.3971536	0.0771	0.0024	
24	205LS1	G70	dark	15.5	38	5.11	29.6	11.6	21.7	34.4	12.46	217	100.6	604	170.2	1944	392	0.00368	12.87001	0.3809656	0.1138	0.0061	
25	205LS1	G29	dark	0.723	5.13	0.639	4.82	1.77	1.03	3.63	1.02	21.3	18.2	189	77.6	1107	271	0.00037	13.40483	0.3953166	0.0698	0.0027	
26	205LS1	G83	dark	<MDL	0.638	0.265	4.34	7.57	2.76	26.8	7.51	79.6	31.6	203	78.3	1230	342	0.00592	14.04494	0.4142469	0.0613	0.0032	
27	205LS1	G8	dark	4.1	12.8	1.42	8.5	1.89	0.51	2.4	0.672	15.2	18.28	361.8	248.1	4610	1078	0.0013	13.45895	0.380401	0.087	0.0033	
28	205LS1	G15	dark	1.19	4.5	0.625	4.72	3.18	4.2	16.1	9.22	222	149.5	1233	414	5240	1343	0.00153	13.83126	0.3634771	0.05679	0.0018	
29	205LS1	G13	dark	<MDL	0.0042	<MDL	<MDL	0.0036	0.066	0.546	0.674	15.13	9.39	89.8	42.94	852	223.6	0.00015	13.51351	0.3469686	0.0613	0.003	

Table A5 – IV: (Continued)

30	205LS1	G16	dark	12.26	51.5	8.56	66.6	16.8	10.3	22.5	1.94	20.49	19.18	242	106	1649	517	0.00105	13.60544	0.4257485	0.0617	0.002
31	205LS1	G10	dark	0.69	3.65	0.653	5.59	1.77	0.384	3.1	1.095	29.01	23.14	215.9	75.1	951	238.3	0.00162	14.10437	0.3779733	0.0674	0.0026
32	205LS1	G22	dark	11.5	38.4	5.88	35	8.6	7.5	18.7	8.58	188.3	113.3	797	223.6	2302	456	0.0018	14.22475	0.4046871	0.0691	0.0026
33	205LS1	G48	dark	10.37	125	9.9	77.5	33.9	17.3	48.4	6.51	64.1	35.1	318.2	118.7	1567	365.4	0.00222	13.42282	0.432413	0.0784	0.0027
34	205LS1	G50	dark	4.51	14.5	2.12	12.47	1.8	0.679	2.2	0.55	13.49	18.99	636	627	13170	3300	0.00062	13.55014	0.4590154	0.0786	0.0036
35	205LS1	G25	dark	4.35	5.95	1.82	9.99	5.63	3.41	21.3	10.24	184.4	95.2	633	179.3	2008	386	0.02604	13.55014	0.4222942	0.0827	0.0039
36	205LS1	G27	dark	22.1	67	8.1	58	23.2	49.6	61.9	14.4	199	89	553	150.7	1768	359	0.00663	13.29787	0.4420835	0.0882	0.0045
37	205LS1	G14	dark	66.8	221	29.1	161	30.1	17.7	39.2	5.02	46.6	29.3	340	147.1	2153	605	0.00313	13.49528	0.3824572	0.0971	0.0046
38	205LS1	G9	dark	16.6	144	11.9	89.8	29.5	21.8	48.8	6.56	74.9	42.2	342	115.4	1459	336.7	0.00787	12.9199	0.400617	0.1389	0.0087
39	205LS1	G54	dark	1.74	8	1.02	5.6	2.6	1.9	20	10.6	194	96	590	172	2020	510	0.00714	15.10574	0.7073685	0.05441	0.0017
40	205LS1	G57	dark	0.063	0.451	0.0425	0.376	0.229	0.195	1.84	1.13	25.1	19.6	261	150	2700	611	0.00904	14.66276	0.4299929	0.0648	0.0025
41	205LS1	G6	dark	0.46	4.2	0.73	10.4	17.3	9.87	72	24.52	287	103.1	556	191.8	2850	672	0.01506	13.96648	0.3901252	0.087	0.0028
42	205LS1	G81	dark	<MDL	<MDL	<MDL	<MDL	0.1	0.162	2.1	1.18	23.27	12.05	84.9	25.23	293.4	59.5	0.0001	14.0647	0.3956314	0.0855	0.0036
43	205LS1	G2_1	dark	0.76	1.72	0.237	1.2	0.217	0.079	0.454	0.116	5.61	15.5	458	337	6760	1880	0.00017	14.90313	0.3997859	0.0641	0.0022
44	205LS1	G28	dark	3	2.07	0.327	1.45	0.41	0.241	1.23	0.537	12.1	7.4	51.7	16.1	208	47.9	0.0101	13.64256	0.4839109	0.1126	0.0077
45	205LS1	G30	dark	1.21	5.6	0.75	4.61	0.96	0.192	1.45	0.79	32.5	37.7	512	254.9	3770	951	0.00068	14.70588	0.4108997	0.05877	0.0018
46	205LS1	G41	dark	7	11.7	1.28	6.8	1.71	0.373	3.12	1.23	38.2	35.4	429	193	3150	780	0.00071	14.51379	0.5266251	0.0776	0.0032
47	205LS1	G5	dark	5.87	10.98	2.2	10.37	2.3	1.28	6.34	2.71	56.3	33.9	243	71.4	822	197.9	0.01869	13.69863	0.3940702	0.1261	0.0065
48	205LS1	G18	dark	1.34	2.8	0.499	2.8	2.1	1.05	7.6	2.76	49	31.8	275	99.7	1317	358	0.00063	11.45475	0.5510878	0.0894	0.0036
49	205LS1	G29	dark	3.6	11.5	1.58	8.26	1.5	0.632	2.8	1.304	34.1	30.02	344.4	181.9	3747	1226	0.00037	12.40695	0.3540444	0.099	0.01
50	205LS1	G38	dark	6.37	32.4	6.26	51.4	14	4.8	17.1	1.99	32.68	28.82	428	259	4900	1290	0.00917	12.46883	0.3264905	0.1216	0.0062
51	205LS1	G39	dark	47	192	19.2	112	26.3	9.41	33.5	6.25	88.5	54.6	471	178	2680	620	0.00125	12.2549	0.3904748	0.1425	0.0089
52	205LS1	G47	dark	29.8	140	23.5	165	71.9	29	100	14.8	173	92	721	239	2920	568	0.01623	11.48106	0.3031737	0.184	0.013
53	205LS1	G42	Intermediate	<MDL	<MDL	<MDL	<MDL	0.188	0.219	2.94	1.69	29.2	14	95.5	29.85	370	68.5	0.00016	13.6612	0.4479083	0.0782	0.0036
54	205LS1	G76	Intermediate	0.277	1.47	0.221	1.06	0.211	0.205	0.89	0.724	16.43	9.85	86	42.2	841	215.5	0.00019	13.40483	0.4492234	0.0993	0.0096
55	205LS1	G17	Intermediate	0.0108	0.024	<MDL	<MDL	<MDL	<MDL	0.171	0.123	3.48	2.61	27.1	9.1	133	35	0.00552	13.88889	0.3858025	0.0563	0.0021
56	205LS1	G7	Intermediate	0.0079	0.047	0.0033	<MDL	0.031	0.043	1.29	1.407	43.7	38.8	456	245.2	5220	1745	0.00016	13.86963	0.384733	0.0617	0.0033
57	205LS1	G59	Intermediate	0.411	1.51	0.205	1.31	0.37	0.389	1.35	1.003	35.2	32.38	320.3	121.1	1646	374	0.00014	13.88889	0.4050926	0.062	0.0028
58	205LS1	G45	Intermediate	4.73	13.12	1.565	7.94	1.81	0.998	6.62	4.35	116.4	81.8	712	253	3520	790	0.00106	13.36898	0.5361892	0.0673	0.0024
59	205LS1	G58	Intermediate	0.114	0.465	0.058	0.293	0.355	0.177	2.65	1.354	27.04	17.29	156.8	67.2	1154	309	0.00244	13.19261	0.522135	0.0815	0.0072
60	205LS1	G24	Intermediate	2.55	10.3	1.017	5.89	0.73	0.367	3.1	1.98	52.4	35.9	259	80.4	901	187	0.00575	13.1406	0.3626185	0.0671	0.0025
61	205LS1	G40	Intermediate	0.0398	0.076	<MDL	0.029	0.052	0.108	2.37	1.693	41.9	24.95	206	80.5	1320	306	0.00014	12.70648	0.4036366	0.0663	0.0034
62	205LS1	G41	Intermediate	<MDL	0.0237	0.0028	0.021	0.194	0.527	8.7	5.8	109	55	368	114	1280	265	0.00071	13.29787	0.3890335	0.0879	0.0088
63	205LS1	G53	Intermediate	8	142	6.18	39.3	14.8	2.33	17.9	2.64	28.3	14.61	122	51	833	209	0.00917	12.73885	0.4381516	0.1209	0.0087

Table A5 – IV: (Continued)

Data discarded for deviation from weighted average																						
64	205LS1	G35	bright	3.4	9.3	1.37	7.2	0.81	0.355	0.84	0.398	10.27	8.3	93.2	50.2	953	258	0.01222	13.12336	0.7233348	0.1314	0.0072
65	205LS1	G32	dark	7.03	43.6	5.67	44.2	21	9.47	36.5	6.64	66.4	26.75	192.7	71	1091	300.7	0.00581	14.55604	0.4025688	0.1089	0.0044
66	205LS1	G34	dark	71.4	242	38.5	241	48.6	38.6	68.7	11.7	131	55.2	362	113	1440	351	0.02398	13.36898	0.4289514	0.1936	0.0089
67	205LS1	G4	dark	21.6	23.1	7.51	36.7	11	7.03	18.7	5.6	79.3	38.6	264	77.9	969	236.8	0.02874	9.541985	0.3277781	0.27	0.022
68	205LS1	G49	dark	60.5	168	19	100.3	27.1	56.9	57.9	8.54	84.5	43.2	363	131.9	1787	443	0.01155	12.12121	0.4554637	0.2402	0.0098
69	205LS1	G51	dark	35.6	88	10.3	65.3	31	47.2	68.1	9.7	79.9	27.5	178	61.8	814	209.4	0.00307	13.24503	0.4210342	0.1637	0.0074
1500 age group																						
70	205LS1	G43	mixed	0.34	9.3	0.23	2	3.27	0.53	20	7.46	103	44.2	240	63.9	703	144	0.40816	4.079967	0.1664613	0.098	0.0033
950 Ma age group																						
71	205LS1	G55	bright	0.0115	33.96	0.092	1.9	4.13	0.973	23.8	7.36	89.2	30.2	133.4	28.7	256	44.5	0.64144	6.024096	0.1524169	0.0691	0.0029
72	205LS1	G79	bright	0.065	34.49	0.222	3.51	6.5	1.303	28.6	8.79	101.1	34.8	157.8	33.5	293.2	54.6	0.42194	6.480881	0.1764077	0.0716	0.0024
470 Ma age group																						
73	205LS1	G52	bright	0.181	0.399	0.047	0.216	0.117	0.123	1.57	1.34	35.3	25.7	236.9	93.7	1352	311.1	0.00074	12.62626	0.573921	0.0592	0.0022
74	205LS1	G33	dark	2.8	13.8	2.2	14.8	4.9	3	8.1	2.45	56.4	54	606	244.3	3600	901	0.00037	13.08901	0.3769085	0.05658	0.0017
75	205LS1	G46	dark	<MDL	<MDL	0.0018	<MDL	0.023	0.045	0.51	0.409	10.09	7.48	91.3	60.6	1262	313.6	0.00014	13.0039	0.355113	0.0567	0.002
600 Ma age group																						
76	205LS1	G23	mixed	0.0155	7	0.0091	0.13	0.159	0.082	0.85	0.571	14	14.78	201	87	1340	334	0.19231	10.41667	0.7595486	0.0628	0.0024
77	205LS1	G23	dark	<MDL	10.4	0.061	0.93	1.8	0.59	10.3	3.2	39	18.3	124	36.8	476	112	0.19231	9.90099	1.764533	0.0663	0.0046
510 Ma age group																						
78	205LS1	G104	dark	125	177	32	153	38.2	23.6	47.6	7.6	67.2	26.6	192	62.4	782	194	0.01163	5.434783	0.5612004	0.525	0.044
79	205LS1	G104	bright	90	137	21.4	104	25.6	14.8	32.6	4.34	35.1	13	93	31.7	410	107	0.01163	3.076923	0.1893491	0.71	0.023