

Durham E-Theses

Metal enrichment in pegmatites: insights from Mataketake Region, New Zealand

William J. Nicholson

How to cite:

Nicholson, William J. (2026) Metal enrichment in pegmatites: insights from Mataketake Region, New Zealand. Masters thesis, Durham University.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:

- a full bibliographic reference is made to the original source
- a <https://etheses.durham.ac.uk/id/eprint/16574/> is made to the metadata record in Durham E-Theses
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the [full Durham E-Theses policy](#) for further details.

**Metal enrichment in pegmatites: insights from Mataketake
Region, New Zealand**

William J.Nicholson

Earth Sciences, Masters by Research

Department of Earth Sciences

Durham University

2025

Abstract

The use of lithium in high-capacity energy storage systems and rechargeable lithium-ion batteries has made it a necessary component to facilitate the energy transition. Hard-rock sources such as pegmatites and lithium-enriched granites comprise a significant portion of economic lithium resources and are commonly derived from anatexis of metamorphic rocks. Crustal melting, via mica dehydration reactions, is assumed to be a driving factor in the enrichment of lithium. However, the specific mechanisms and reactions that control lithium mobilisation and enrichment are not well constrained. This research intends to enhance knowledge on the mechanisms for lithium enrichment using samples of Alpine Schist and Mataketake Pegmatite (New Zealand) as a case study. Through in-situ petrological analysis of mineralogy, textures, and micro-textures, followed by geochemical analyses of mica and feldspar compositions we aim to establish melting reactions, mechanisms, and processes, including which phase(s) are melting and availability of fluids. Deformation textures are abundant in the pegmatite, in the form of fractured porphyroblasts, mica-fish, kink-banding, sub-grain deformation, deformation twinning, and highly disequilibrium inclusion textures, often occurring as 'strings of beads', interpreted as annealed myrmekite. This results in a protomylonitic texture within the pegmatite. Therefore, the intersection of strain and low-degree melting exert dominant controls on the petrography, and consequently will have important implications for the geochemistry. Using Laser Ablation ICP-MS, we supplement these observations using texturally constrained analysis of major and trace elements in key phases, such as micas and feldspars, to understand elemental concentrations in the Alpine Schist and the produced melt (Mataketake Pegmatite). We apply an empirical Ti-in-biotite geothermometer to constrain biotite closure temperatures within analysed samples. This thesis suggests a temperature range of 539-635°C and is consistent with existing thermometry for crustal anatexis associated with the Mataketake Pegmatites. This is important as it removes the possibility for biotite melting, which initiates ~740°C (Kunz et al., 2022). We calculate whole-rock Sr, Rb and Ba and normative Ab-An-Or composition for the Alpine Schist and Mataketake Pegmatite. Our data align with recent literature and suggest H₂O-present muscovite dehydration melting. Modelling of major elements K, Fe and Mg, followed by trace elements Sr, Ba, Pb, La and Li, intends to further constrain melting scenarios. Within the analysed system, K is solely hosted in significant quantities in micas, which therefore make them vital in determining melt concentrations of K. With the possibility for biotite melting in notable proportions inhibited, we look to accessory phases to aid in sufficient enrichment of Fe and Mg. This modelling therefore facilitates the refining of possible melting reactions to include accessory phases containing Fe and Mg. Trace element modelling further confines the proposed reaction. With Ba contents elevated in muscovite (averaging 2607ppm in the schist), this limits the extent of muscovite breakdown. Like our major element modelling, our trace element modelling points to the inclusion of accessory phases in the melting fraction, notably monazite and epidote for the liberation of La. Using all evidence, we propose that a low-temperature, fluid-present muscovite dehydration partial melt has formed the Mataketake Pegmatite. We finalise

our proposed melting reaction as: Muscovite + Quartz + Plagioclase (Ab) + H₂O $\pm$ (garnet) $\pm$ (epidote) $\pm$ (monazite) $\pm$ (chlorite) $\pm$ (ilmenite) = melt. Our proposed reaction contains muscovite, quartz and plagioclase as the melting phases, and aligns with the observed depletion in Li in the pegmatite relative to the schist, with calculated whole rock Li concentrations at 34.7ppm (Alpine Schist) and 21.5ppm (Mataketake Pegmatite). This is due to the melting phases hosting insufficient Li. Achieving Li enrichment would require biotite melting, which is inhibited by temperature constraints. Additionally, fluid-presence limits the extent of muscovite melting, which contains Li in higher quantities than quartz and plagioclase. We highlight the necessity for sufficient melting of micas, particularly biotite, for enrichment in unfractionated melts. We consider other analysed metals, (e.g., V, Cs and W), which are enriched in the Alpine Schist relative to the produced pegmatite. Integrating this work with previous literature, this can be explained by the absence of higher temperature melting reactions, particularly biotite breakdown, which facilitate enrichment of critical metals. This aids understanding of the processes dictating how lithium, and other trace elements, are mobilised during partial melting. Identifying the key controls on lithium enrichment and improving understanding of the mobilisation of lithium has significant implications for understanding the links between hard-rock lithium resources and geothermal fluids, which is vital for the development of mineral-deposit models and facilitating the transition to renewable energy sources.

Table of Contents

Abstract.....	2
Table of Contents	4
List of Tables	6
List of Figures	8
Context.....	11
Declaration.....	12
Statement of Copyright.....	12
Acknowledgements.....	12
Data	12
1 INTRODUCTION	13
1.1 Crustal Melting.....	13
1.2 Pegmatites.....	14
1.3 Socio-economic Importance of Pegmatites	16
1.3.1 Importance of Pegmatite-Associated Elements.....	16
1.3.2 Lithium's Association with Pegmatites.....	16
1.4 Case Study Approach	17
1.5 Thesis Aims.....	18
1.7 Why the South Island, New Zealand?.....	19
1.8 Thesis Structure	19
Chapter 2.....	19
Chapter 3.....	20
Chapter 4.....	20
Chapter 5.....	20
Chapter 6.....	20
Chapter 7.....	21
2 GEOLOGICAL SETTING	22
2.1 Geological Background of New Zealand.....	22
2.1.1 Tectonics and Regional Setting.....	22
2.1.2 The Southern Alps; Background and Structure	24
2.2 Metamorphism in South Island, New Zealand.....	25
2.2.1 Torlesse Terrane, Haast Schists and the Alpine Hanging Wall	27
2.3 The Mataketake Pegmatites	31
2.3.1 Location	31
2.3.2 Formation.....	32
2.3.3 Petrology of Mataketake Pegmatites.....	35
3 METHODOLOGY	37

3.1 Hand Specimen & Petrological Analyses	37
3.2 SEM Analyses.....	38
3.2.1 Imaging	38
3.2.2 Geochemical Analysis.....	38
3.2.2.1 EDS Data Processing	38
3.3 Geochemical mapping	39
3.4 Compositional Quantification Using Aztec	39
3.4.1 Geochemical Mapping Uncertainty	41
3.5 Laser ablation ICP-MS Analyses.....	42
3.5.1 Laser-ICP-MS Data Processing	42
3.5.2 Laser Ablation ICP-MS Error/Uncertainty	42
3.6 Data Processing & Calculations.....	43
4 PETROLOGY	45
4.1 Alpine Schist; Chlorite-Zone/Lower-Greenschist Facies	45
Chlorite Schist (from the Callery Tributary) (AS.Cal (+bt))	45
Otago Chlorite Schist (Ot.Cl.1 & Ot.Cl.2).....	48
4.2 Alpine Schist; Upper Greenschist Facies/Low Amphibolite Facies	54
Hare-Mare Biotite-Garnet (1.AS.H)	54
Alpine Schist: Mataketake Pegmatite Boundary Sample (A – 1.AS & AS.MP.B)	63
4.3 Mataketake Pegmatite (1(B) MP & 2MP.1)	74
4.4 Summarising Key Textures and Interpretations.....	97
5 MINERAL GEOCHEMISTRY	99
5.1 Mineralogical Abundances	99
5.1.2 Minor Phases.....	99
5.2 Major Element	103
5.2.1 Plagioclase	103
5.2.2 Muscovite.....	105
5.2.3 Biotite.....	107
5.3 Trace Elements.....	110
5.3.1 Plagioclase	110
5.3.2 Muscovite.....	112
5.3.3 Biotite.....	114
5.4 Limitations – Input into methods.	118
6 DISCUSSION	120
6.1 Formation of Mataketake Pegmatites	120
6.1.1 Basic Geochemical Observations.....	120
6.1.2 Constraining Temperature.....	124

6.1.3 Melt Processes, Reactions and Composition	135
6.1.4 Summarising Melt Reactions and Processes.....	151
6.2 How does this link to metal enrichment.....	152
7 SYNTHESIS AND CONCLUSIONS	158
Section 1: Conclusions relevant to the formation of the Mataketake Pegmatites.....	158
Section 2: Conclusions relevant to metal enrichment.....	159
Section 3: Suggestions for future work.....	160
8 Bibliography	162

List of Tables

Table ID	Caption	Pages
Table 1.1	5 Classes of Granitic Pegmatites (Černý et al., 2005)	15
Table 2.1	Geochronological indicators for the Alpine Schist	29
Table 3.1	Trace elements analysed for each mineral, their dwell times (s), and the date of analyses	43
Table 5.1	Mineralogical Composition of Alpine Schist (1.AS) and Mataketake Pegmatite (1(B)MP.	99
Table 5.2	Garnet Average Compositions	100
Table 5.3	Epidote Average Compositions	100
Table 5.4	(Fluor)Apatite Average Compositions	100
Table 5.5	Apatite Average Compositions	101
Table 5.6	Titanite Average Compositions	101
Table 5.7	Fe-Oxide Average Compositions	101
Table 5.8	Average Chlorite Compositions	101
Table 5.9	Zircon Average Compositions	102
Table 5.10	Average Ilmenite Composition	102
Table 5.11	Average Zeolite Composition	102
Table 5.12	Average Monazite Composition	102
Table 5.13	Mean anorthite content of plagioclase feldspars in Alpine Schist (1.AS), Mataketake Pegmatite (1(B)MP, and Alpine Schist from Hare Mare Creek (1.AS.H)	103
Table 5.14	Average mica compositions in 1(B)MP, 1.AS and 1.AS.H (wt% oxide)	108
Table 5.15	Plagioclase Minor and Trace Elements for each sample. Mean calculated from data above limits of detection (LOD).	111
Table 5.16	Muscovite minor and trace element composition. Mean calculated from data above limits of detection (LOD).	113
Table 5.17	Biotite minor and trace element composition. Mean calculated from data above limits of detection (LOD).	115
Table 6.1	Average uncertainties as a percentage of average composition for Sr, Rb and Ba	123
Table 6.2	Summary of calculated biotite temperatures for each rock sample.	126
Table 6.3	Relevant data and parameters and thermometry calculations for biotite temperatures after Henry et al., (2005).	126

Table 6.4	Melting reactions from literature which coincide with conditions for the Mataketake Pegmatite	136
Table 6.5	Scenarios involving melting of micaceous material relative to the quantity of K ₂ O, FeO and MgO necessary to precipitate a pegmatite with 19.4% muscovite and 7.6% biotite.	141
Table 6.6	Modelled equations for melt composition.	142
Table 6.7	Range of apparent plagioclase-melt partition coefficients	143
Table 6.8	Range of trace element melt concentrations calculated using a range of apparent partition coefficients	143
Table 6.9	Modelled equations for melt composition (ppm), using apparent K _d Coefficients from the literature	143
Table 6.10	Melt scenarios for the apparent partition coefficient obtained from literature. *denotes very close to satisfying system	144
Table 6.11	Mineral-melt partitioning calculations for muscovite and biotite data obtained from Laser ICP-MS.	147
Table 6.12	Expressions for mass-balance modelling where a, b, c & d are the modal abundances of plagioclase, biotite, muscovite and quartz respectively. Liquid contents (Li) calculated using partition coefficients in Table 6.11. Coefficients for each phase taken from average Li abundance in Alpine Schist in each phase. The 2 different equations correspond to calculated melt contents from muscovite and biotite.	147

List of Figures

Figure ID	Caption	Pages
Figure 2.1	A) a) tectonic setting of New Zealand's South Island. b) Map showing Haast Schists (Alpine and Otago Schists) and Marlborough Schist locations.. B) schematic cross section across South Island	23
Figure 2.2	Simplified geological map of key metamorphic terranes	27
Figure 2.3	Map of South Island, New Zealand and the study region	32
Figure 2.4	A) Rb/Sr vs Ba for whole-rock analyses of 12 pegmatite samples from the South Island, New Zealand. (Briggs & Cottle, 2018) B) Briggs and Cottle (2018); An-Ab-Or normative ternary plot.	34
Figure 3.1	Map of South Island, New Zealand showing sample locations	37
Figure 3.2	Electron Images showing method for constraining mica abundance.	40-41
Figure 4.1	Chlorite Schist from the Callery Tributary, with intruding quartz veins.	46
Figure 4.2	AS.Cal 80um Thick Section Scan.	47
Figure 4.3	Ot.Cl.1 – Otago Chlorite Schist from the Manukerikia region.	48
Figure 4.4	Ot.Cl.2 Alternative view to Figure 4.3	49
Figure 4.5	Ot.Cl.2 –Orthogonal view to Figure 4.3, looking at the surface of the fabric.	49
Figure 4.6	Photomicrograph of Ot.Cl.2 PPL (Left) and XPL (Right).	50
Figure 4.7	Photomicrograph of Ot.Cl.2 in PPL (left) and XPL (right).	50
Figure 4.8	SEM image of Otago Schist (Ot.Cl.2 SEM003).	51
Figure 4.9	Electron Image of Otago Schist (Ot.Cl.2 SEM006)	52
Figure 4.10	Electron Image of Otago Schist (Ot.Cl.2 SEM008).	52
Figure 4.11	Electron Image of Otago Schist (Ot.Cl.2 SEM010), displaying varying domains of mineralogy and textures.	53
Figure 4.12	Hand specimen photo of 1.AS.H.	54
Figure 4.13	Photomicrographs of 1.AS.H, with PPL (left) and XPL (right) 80µm 'thick' section.	56
Figure 4.14	Photomicrograph 1.AS.H, with PPL (left) and XPL (right) of 80µm 'thick' section displaying the varying domains observed.	56
Figure 4.15	Photomicrographs in PPL (left) and XPL (right) 80µm 'thick' section, illustrating the key constituents and holistic textural variation in 1.AS.H.	57
Figure 4.16	Photomicrographs (1.AS.H Thin 001) in PPL (left) and XPL (right) from 40µm 'thin' section.	57
Figure 4.17	Photomicrographs (1.AS.H Thin 002) in PPL (left) and XPL (right) from 40µm 'thin' section.	58
Figure 4.18	Photomicrographs (1.AS.H Thin 004) in PPL (left) and XPL (right) from 40µm 'thin' section.	58
Figure 4.19	Electron Image (1.AS.H.002)	59
Figure 4.20	Electron Image (1.AS.H.003)	60
Figure 4.21	Electron Image (1.AS.H.010)	61
Figure 4.22	Electron Image (1.AS.H.019).	61
Figure 4.23	Electron Image (1.AS.H.042)	62
Figure 4.24	Electron Image (1.AS.H.019).	63
Figure 4.25	1.AS (top) & 1(B)MP (bottom) Hand Specimen.	64
Figure 4.26	1.AS 80um Thick Section Scan.	65
Figure 4.27	1.AS.MP.B 80um Thick Section Scan.	66
Figure 4.28	PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section).	67
Figure 4.29	PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section).	67

Figure 4.30	PPL (left) and XPL (right) of 1.AS.MP.B.2 (80µm Section).	67
Figure 4.31	PPL (left) and XPL (right) of 1.AS.MP.B.3 (80µm Section).	68
Figure 4.32	PPL (left) and XPL (right) of 1.AS.MP.B.4 (80µm Section).	69
Figure 4.33	PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section).	69
Figure 4.34	PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section).	69
Figure 4.35	PPL (left) and XPL (right) of 1.AS.1 (80µm Section).	70
Figure 4.36	PPL (left) and XPL (right) of 1.AS.3 (80µm Section).	70
Figure 4.37	PPL (left) and XPL (right) of 1.AS.4 (80µm Section).	70
Figure 4.38	Back-scattered electron Image of Alpine Schist (1.AS.001).	71
Figure 4.39	Back-scattered electron Image of Alpine Schist (1.AS.003).	71
Figure 4.40	Back-scattered electron Image of Alpine Schist (1.AS.005).	72
Figure 4.41	Back-scattered electron Image of Alpine Schist (1.AS.018).	72
Figure 4.42	Back-scattered electron Image of Alpine Schist (1.AS.031).	73
Figure 4.43	Montaged electron images of Alpine Schist and Mataketake Pegmatite boundary (1.AS.MP.B Area 2).	74
Figure 4.44	Mataketake Pegmatite hand specimen (2MP.1).	75
Figure 4.45	From (Vernon, 2018); showing the dominant effect that structurally anisotropic micas (red) can have on a quartz (white) – mica rock.	76
Figure 4.46	2MP.1 (40µm Section) No.001	77
Figure 4.47	2MP.1 (40µm Section) No.003	77
Figure 4.48	2MP.1 (40µm Section) No.005	79
Figure 4.49	2MP.1.02 (80µm section)	80
Figure 4.50	2MP.1.07 (80µm section)	81
Figure 4.51	2MP.1.05 (80µm section)	81
Figure 4.52	2MP.1.08 (80µm section)	82
Figure 4.53	2MP.1.10 (80µm section)	82
Figure 4.54	2MP.1.17 (80µm section)	83
Figure 4.55	2MP.1.20 (80µm section)	83
Figure 4.56	2MP.1.23 (80µm section)	84
Figure 4.57	2MP.1.24 (80µm section)	84
Figure 4.58	2MP.1.26 (80µm section)	85
Figure 4.59	2MP.1.34 (80µm section)	85
Figure 4.60	Back-scattered electron Image of Mataketake Pegmatite (2MP.1.007).	86
Figure 4.61	1(B)MP – Back-scattered electron Image (No.10)	87
Figure 4.62	1(B)MP – Back-scattered electron Image (No.12)	88
Figure 4.63	1(B)MP – Montaged Back-scattered Electron Images (No.9)	89
Figure 4.64	1(B)MP – Montaged back-scattered Electron Image (No.6&8; Area 1)	90
Figure 4.65	1(B)MP – Montaged back-scattered Electron Image (No.13; Area 3)	91
Figure 4.66	1(B)MP – Montaged Back-scattered Electron Image (No.14; Area 4)	92
Figure 4.67	Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.025).	93
Figure 4.68	Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.027).	93
Figure 4.69	Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.031).	94
Figure 4.70	Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.035).	95

Figure 4.71	Back-scattered Electron Image of Mataketake Pegmatite (1.AS.MP.B 001).	96
Figure 4.72	Back-scattered Electron Image of Mataketake Pegmatite (1.AS.MP.B 002).	97
Figure 5.1	Anorthite content of plagioclase compositions within analysed rock samples.	104
Figure 5.2	Albite grain rimmed by oligoclase, from Newton Range (Murphy, 2010).	104
Figure 5.3	Top: Muscovite compositions plotted on mgli v feal, after Tischendorf et al. (2007); Tischendorf et al. (2004). Bottom: Close-up of muscovite compositions in the pegmatite (1(B)MP) and Alpine Schist (1.AS).	106
Figure 5.4	Muscovite compositions (1.AS, 1(B)MP and those from nearby Newton Range (Murphy (2010)) relative to identified compositions of Otago Schist and Alpine Schist muscovites (Little et al., 1999).	107
Figure 5.5	Fe v Al (wt%) EDS data, showing two compositional clusters for Fe and Al within 1(B)MP.	109
Figure 5.6	Biotite compositions on Al (IV) vs Mg/(Mg+Fe) plot. A: EDS data. B: Laser-ICP data.	109
Figure 5.7	Biotite compositions after (Tischendorf et al., 2007; Tischendorf et al., 2004).	110
Figure 5.8	A: Xan v Sr (ppm). B: Xan v Pb (ppm). C: Xan v Ba (ppm). These three scatter plots illustrate the 3 different compositions of the plagioclases within samples.	111
Figure 5.9	Muscovite geochemistry, showing 2 distinct compositions.	114
Figure 5.10	V (ppm) v Cr (ppm) within biotite..	116
Figure 5.11	Ti wt% v Nb ppm in biotite grains.	117
Figure 6.1	Left: Briggs and Cottle (2018), showing whole rock compositions of Ba (ppm) against Rb/Sr for the Alpine Schist and Mataketake Pegmatites. Right: This Study, showing whole rock compositions of Ba (ppm) against Rb/Sr for the Alpine Schist and Mataketake Pegmatite.	123
Figure 6.2	Calculated biotite crystallisation T°C after Henry et al (2005), against Ti (a.p.f.u).	128
Figure 6.3	Recorded and proposed temperatures in literature for rock samples within the Mataketake Range and surrounding regions	132
Figure 6.4	Beyssac et al. (2016) constrain metamorphic temperatures along the Alpine Fault.	134
Figure 6.5	Normative An-Ab-Or data (whole-rock) for a suite of Mataketake Pegmatites.	139
Figure 6.6	Petrologic modelling of Li melt concentrations from metasedimentary protoliths, and remelting of corresponding granites produced	154
Figure 6.7	Whole rock analyses of different regions of migmatite samples	157

Context

This thesis originally intended to look at elemental progression through the Barrovian metamorphic facies of South Island, New Zealand, with a focus on lithium and other critical metals. Hence, samples were originally chosen to cover the complete spread of metamorphic facies: from the low-grade chlorite schists that are distal to the Alpine Fault, to the biotite-garnet schists and Mataketake Pegmatites that are closer. Notable time was therefore spent analysing the whole range of these samples. However, due to ill health, the supervisory team changed from early 2024. Additionally, following the initial petrographic analyses of the range of these samples, it was realised that the grain size in samples from the lower metamorphic grades were too small to facilitate LA-ICP-MS analyses.

The combination of these two key factors led to a change in the focus of the project to examine local melting processes, for which appropriate analyses could take place. The decision to alter the project to focus on metals enrichment was also informed by the literature review undertaken at the time, notably: Briggs & Cottle (2018), Wallace (1974), Koopmans et al., (2023), Kunz et al (2023).

As many months had been spent analysing the samples of lower-grade metamorphic facies, this work remains part of the thesis. The samples and their analyses also give a greater contextual setting to the thesis, allowing the reader to better understand the mineralogical and textural changes observed within the Alpine Schist facies.

Some of this context is already mentioned in the conclusion section, with some of the original aims included as suggested future research.

Declaration

I declare that this thesis, submitted for the degree of Master of Science at Durham University, is my own work and does not contain material previously submitted for a degree in this or any other institution.

Statement of Copyright

The copyright of this thesis (including any appendices or supplementary materials to this thesis) rests with the author, unless otherwise stated.

© William J. Nicholson 31/05/2025

This copy has been provided under licence to the University to share in accordance with the University's Open Access Policy, and is done so under the following terms:

- this copy can be downloaded for personal non-commercial research or study, without prior permission or charge.
- any quotation from the work (e.g. for the purpose of citation, criticism or review) should be insubstantial, should not harm the rights owner's interests, and must be accompanied with an acknowledgement of the author, the work and the awarding institution.
- the content must not be changed in any way or sold commercially in any format or medium without the formal permission of the author.

Acknowledgements

I would like to express gratitude and acknowledge the work of Dr. Madeleine Humphreys and Dr. Catriona Menzies for their supervision throughout this project. Their expertise and professionalism aided me throughout this project.

Data

Supplementary files:

File	Contents
13.09.24AllDataMatlab	All processed data used for Figures
Biotite Analysis	Analysis on biotite mineral data
Feldspar Analysis	Analysis on feldspar mineral data
Muscovite Analysis	Analysis on muscovite mineral data
Nielsen+Lithium Partitioning Calcs	Partitioning calculations using Nielsen et al. (2017). Other partitioning calculations using a range partition coefficients from the literature, including those for Li.
NormCalculations	Calculations of normative whole rock compositions
Sr Rb Ba Modelling	Whole rock calculations and modelling for Sr, Rb, Rb, La, Li & Pb.
SrBaPbLamassbalance	Mass balance modelling for Sr, Ba, Pb and La
Whole Rock Mineralogy Calcs	Calculations of modal phase abundance

1 INTRODUCTION

1.1 Crustal Melting

Throughout Earth's history, partial melting has been responsible for the irreversible, secular differentiation of the continental crust (Johnson et al., 2021), and was the elementary process by which crust was derived from the mantle to ultimately produce the current tectonic regime which defines the relatively-insignificant section of this planet that is inhabited. Crustal anatexis plays a vital role in plate tectonics (Lourenço et al., 2016; Stern, 2018), orogenic processes (Jamieson et al., 2011), elemental cycling (Chen & Grapes, 2007; Jamieson et al., 2011) and the concentration of economic resources (Černý et al., 2005; Chen & Grapes, 2007; Gardiner et al., 2024; Koopmans et al., 2023; Kunz et al., 2022; Li et al., 2021; Richards, 2018). Crustal melting can result in significant enrichment in metals and Rare-Earth-Elements (REE). Many REE ore deposits are derived from igneous processes (Chen et al., 2024). Porphyry deposits, which are associated intrusive crustal melts, can enrich metals like copper and gold (Feng et al., 2021; Richards, 2018). Within granitic systems (including pegmatites), economic deposits of Li, Rb, Cs, Be, B, P, Sn, Ta, Nb form from crustal melting (Černý et al., 2005; Gardiner et al., 2024; Wolf et al., 2018). As such, crustal melting is a significant geological process that has real impact on humans, and therefore needs to be well understood.

Within the continental crust, Sallet et al. (2023) outline three main melting processes that produce granitic melts:

- 1) Fluid-absent biotite and amphibole dehydration melting, which occurs between 850 and 900 °C (Michaud et al., 2021; Patiño Douce & Beard, 1995; Peterson et al., 1991; Pickering & Johnston, 1998; Sallet et al., 2015; Sallet et al., 2023; Skjerlie & Johnston, 1993, 1996; Thompson, 1982; Vielzeuf & Holloway, 1988);
- 2) Fluid-absent muscovite dehydration, between 650-700°C (Anenburg & Katzir, 2014; Brearley & Rubie, 1990; Castro et al., 2000; Dyck et al., 2020; Gardien et al., 1995; Michaud et al., 2021; Patiño Douce & Harris, 1998; Sallet et al., 2023; Storre, 1972), and
- 3) Fluid-present partial melting, between 600-700°C (Acosta-Vigil et al., 2006; Beard & Lofgren, 1991; Beard et al., 1994; Carroll & Wyllie, 1990; Gardien et al., 2000; Genier et al., 2008; Holtz & Johannes, 1991; Sallet et al., 2015; Sallet et al., 2023; Sawyer, 2010; Weinberg & Hasalová, 2015)

Differentiating between these different melting processes is important because it can help control the concentrations of metals released during partial melting (e.g. Koopmans et al. 2023).

Fluid-present melting can be divided into congruent and incongruent H₂O-present melting. The latter typically occurs at higher temperatures, with the produced melt being water undersaturated (Weinberg & Hasalová, 2015). These two H₂O-present reactions can be distinguished through the precipitation of

peritectic phases, which incongruent melting will generate (Conrad et al., 1988; Gardien et al., 2000; Icenhower & London, 1995; Patiño Douce & Harris, 1998; Weinberg & Hasalová, 2015). Most frequently, this peritectic phase is amphibole, but garnet, cordierite, pyroxenes and aluminosilicates can also precipitate as peritectic minerals (Conrad et al., 1988; Gardien et al., 2000; Icenhower & London, 1995; Patiño Douce & Harris, 1998; Weinberg & Hasalová, 2015).

Fluid-absent melting typically involves dehydration melting reactions of muscovite, biotite or amphibole (Weinberg & Hasalová, 2015). Fluid-absent muscovite dehydration reactions, occurring between ~650-700°C will generate melts of peraluminous composition, and generally precipitate aluminosilicates/K-feldspar as a peritectic phase (Patiño Douce & Harris, 1998; Storre, 1972; Weinberg & Hasalová, 2015). Consequently, the identification of peritectic phase(s) is a significant petrographic consideration, due to their use in indicating underlying melting reactions. Dyck et al. (2020) highlight how fluid-absent muscovite dehydration of metasediments produces K-feldspar, sillimanite, and monzogranitic melts. Conversely, fluid-saturated melting does not necessarily precipitate K-feldspar, although melt crystallisation means it is possible (Dyck et al., 2020). As such, the presence/absence of potassic feldspar can be used to infer melting type.

Fluid-absent and -present melting also differ in other ways. Inger and Harris (1993) highlight how melting reactions associated with mica dehydration melting are likely reliant on a temperature overstep to satisfy activation energy requirements (Brearley & Rubie, 1990). Additionally, during dehydration melting reactions, hydrous phases (such as micas) supply H₂O via incongruent breakdown (Patiño Douce & Harris, 1998). As such, in muscovite dehydration melting, muscovite is consumed to a greater extent than plagioclase (Patiño Douce & Harris, 1998). Conversely, more plagioclase is consumed than muscovite in fluid-present scenarios due to the plagioclase + quartz solidus being more intensely depressed, while micas remain stable for longer (Inger & Harris, 1993; Patiño Douce & Harris, 1998; Sallet et al., 2018; Sallet et al., 2023; Weinberg & Hasalová, 2015). Therefore, the composition of produced melts can indicate fluid-absent or -present melting through the relative proportions of plagioclase and muscovite.

In summary, these melting types, their requisite reactions, and products are vital considerations for pegmatite production. They are also important for metal enrichment, as the preferred breakdown of distinct phases may result in the liberation or sequestration of metals.

1.2 Pegmatites

A pegmatite is defined as “an essentially igneous rock that is distinguished from other igneous rocks by its extremely coarse but variable grain size, or by an abundance of crystals with skeletal, graphic, or other strongly directional growth habits” (London, 2008). Previously, Černý (1990) and Černý (1991) divided pegmatites into three petrogenetic classes: Lithium-Caesium-Tantalum (LCT), Niobium-Yttrium-Fluorine (NYF), and ‘mixed’. This followed an earlier classification by Ginsburg et

al. (1979), who separated pegmatites into four classes based on the intrusion depth, and more generally their crustal environment (including relationship to granitic plutons and metamorphism) (Černý et al., 2005). These four classes were: abyssal, muscovite, rare-element, and miarolitic. The three petrogenetic families (LCT, NYF and mixed) of Černý (1990), and Černý (1991), were then revised in 2005 due to uncertainties/misconceptions in its application (Černý & Ercit, 2005), and a review by Ercit (2005), which highlighted poor representation of abyssal- and muscovite-class pegmatites. This revamp classified pegmatites into 5 key classes, of which subclasses do exist (based on REE), however they are not relevant to this study (Table 1.1) (Černý et al., 2005; Černý & Ercit, 2005). Within this case study, the analysed pegmatites do not have a relationship with a granitic body, and consequently the relevant classes, according to Černý and Ercit (2005) are abyssal and muscovite. This gives an inclination into temperature and pressure ranges that possibly led to anatexis.

Table 1.1: 5 Classes of Granitic Pegmatites – from (Černý et al., 2005).

Class	Typical Minor Elements	Metamorphic Host Rocks	Relationship to Granites	Structural Features
Abyssal	U, Th, Zr, Nb, Ti, Y, REE, Mo; rarely Be, B; poor (to moderate) mineralisation	(Upper amphibolite to) low to high P granulite facies; ~400-900MPa, ~700°C-800°C	None(?) (segregations of anatectic leucosomes?)	Conformable to mobilised crosscutting veins
Muscovite	Mineralisation absent: micas and ceramic minerals	High P, Barrovian amphibolite facies (kyanite-sillimanite) ~500-800MPa, ~650°C-580°C	None (anatectic bodies) to marginal and exterior	Quasiconformable to crosscutting
Muscovite-rare element	Li, Be, Y, REE, Ti, U, Th, Nb>Ta; rarely Li, Be; poor mineralisation	Moderate to high P, (T) amphibolite facies; 300-700MPa, ~650°C-520°C	Interior to exterior; poorly defined	Quasiconformable to crosscutting
Rare-element	Li, Rb, Cs, Be, Ga, Sn, Hf, Nb-Ta, B, P, F, or Be, Y, REE, U, Th, Nb>Ta, F; poor to abundant mineralisation; gemstock; industrial minerals	Low-P, Abukuma amphibolite (to upper greenschist) facies (andalusite-sillimanite); ~200-400MPa, ~650-500°C	(Interior to marginal to) exterior	Quasiconformable to crosscutting
Miarolite	Li, Be, B, F, Ta>Nb, or Be, Y, REE, Ti, U, Th, Zn, Nb>Ta, F; poor mineralisation; gemstock	Shallow to subvolcanic; ~100-200MPa	Interior to marginal	Interior pods and crosscutting dikes

1.3 Socio-economic Importance of Pegmatites

1.3.1 Importance of Pegmatite-Associated Elements

Pegmatites can host a wide variety of mineral deposits (Černý et al., 2005; Černý & Ercit, 2005). Their association with metallic elements considered vital for current technologies, particularly Li, Sn, Co, W, Nb and Ta, has catapulted geological and geopolitical interest in pegmatites. For Li and Co, it is their application in rechargeable “Lithium-ion” batteries that has driven significant demand as many governments intend to phase out fossil-fuels. The use of Sn in Li-ion batteries is also increasing, and new technologies such as Na-ion batteries elevate Tin’s importance (USGS, 2025a). Tungsten has a varied range of uses, but notably its application in cemented carbides within construction, metalworking and mining drives demand (USGS, 2025b). Ta and Nb have vital uses in preventing corrosion, electronics and alloys (Mackay & Simandl, 2014). Additionally, other metals such as Be, V, In, and Cs are considered critical (USGS, 2025a), and are often enriched in pegmatites (Kunz et al., 2022).

Shifting energy systems towards ‘green’ alternatives, coupled with an increasingly volatile, tense, and protectionist globe, has resulted in supply security shaping current geopolitics (Riofrancos, 2025). However, the processes and mechanisms that lead to the enrichment of these metals within pegmatites remain “enigmatic” (Koopmans et al., 2023). Therefore, furthering understanding of pegmatite formation and metal enrichment is of utmost pertinence.

1.3.2 Lithium’s Association with Pegmatites

This thesis primarily focuses on contributing to knowledge on lithium enrichment in pegmatites. The formation of Li-pegmatites requires the concentration of the alkali metal via geological processes sufficiently so that Li-ore forming minerals can precipitate, which demands melt concentrations of >5000ppm (Gardiner et al., 2024; Koopmans et al., 2023; London, 1984; Maneta et al., 2015). The mechanisms behind this enrichment are uncertain (Koopmans et al., 2023). Highly evolved peraluminous silicic melts produce Sn- and Li-enriched pegmatites through concentrating incompatible elements and volatiles, such as H₂O, Cl, and F (Gardiner et al., 2024; Simons et al., 2017; Taylor, 1979). This is often thought to occur within the latter stages of magmatic crystallisation (Gardiner et al., 2024). Mineralogically, Li-bearing pegmatites consist of varying proportions of the following assemblage: albite, biotite, muscovite, potassic feldspar and quartz (Gardiner et al., 2024; Koopmans et al., 2023).

Primary Li ore minerals are aluminosilicates, such as petalite (LiAlSi₄O₁₀) and spodumene (LiAl(SiO₃)₂), and micas, for example lepidolite (K(Li,Al)₃(Al,Si,Rb)₄O₁₀(F,OH)₂) and zinnwaldite (KLiFeAl(AlSi₃)O₁₀(OH,F)₂) (Gardiner et al., 2024). Pertinent to metasedimentary rocks, lithium is again primarily hosted in micas (biotite and muscovite), as well as cordierite and staurolite (Knoll et al., 2023; Koopmans et al., 2023; Kunz et al., 2022; Simons et al., 2017). Consequently, muscovite

and biotite act as important sources/sinks of Li in metasediments and pegmatites, and are therefore influential in enrichment during anatexis (Koopmans et al., 2023; Kunz et al., 2022).

Černý (1991), Romer and Kroner (2015), and Romer and Kroner (2016) propose minimum temperature muscovite melting as the mechanism behind Li-enriched pegmatites. This differs from Kunz et al. (2022), who evidence the necessity for biotite breakdown reactions through high-temperature melting to facilitate the liberation of Li (and other metals) into crustal melts. Kunz et al. (2022) also suggest that a protolith lacking muscovite favours Li-enrichment. Koopmans et al. (2023) model melt Li concentrations for a greywacke and a pelitic metasedimentary protolith at 3kbar and 8kbar in fluid-absent and fluxed melting. Their modelling shows that a metasedimentary source attaining Li-concentrations in line with crustal norms cannot produce a melt that is sufficiently enriched to precipitate Li-ore minerals. However, if this produced granitic melt undergoes a second stage of anatexis, then this second-generation melt will attain adequate Li-concentrations to precipitate Li-ore minerals (Koopmans et al., 2023). There is therefore varying proposed mechanisms that result in Li-enrichment in pegmatites, making it an important research area.

The Mataketake Pegmatites manifest a very small fraction in situ melt, and consequently inform on the very earliest stages of melting; the importance of which remains poorly understood. Within these melts, fractionation is often extremely limited, and enrichment in critical metals is therefore confined to protolith composition and breakdown of enriched phases, such as biotite (Černý et al., 2005; Černý et al., 2012; Cerny et al., 1985; Kunz et al., 2022; Wolf et al., 2018). Previous petrologic modelling does not account for lower temperature scenarios (Koopmans et al., 2023), and the constraints that temperature imposes on melting reactions, particularly the limitation of mica melting. Consequently, the Mataketake Pegmatites represent an opportunity to further understand the drivers behind critical metal concentrations in melts and facilitates the refining of the limited literature covering mechanisms behind the critical metal enrichment.

1.4 Case Study Approach

In summary, this case study takes six samples from the natural laboratory that is New Zealand's South Island. Within the relatively young and simple orogeny, these samples span the Barrovian facies, from lower-greenschist chlorite schists, through to lower-amphibolite gneisses. There is a confined region of pegmatitic intrusions, centred around the Mataketake Range, where lower-amphibolite Alpine 'Schists' are intruded. This provides a natural system to analyse petrological, mineralogical and geochemical variation between the Alpine 'Schist' and Mataketake Pegmatite. Previous studies have confirmed the Alpine Schist as the protolith to the pegmatites (Aronson, 1965; Batt et al., 1999; Briggs & Cottle, 2018; Briggs et al., 2018; Cooper et al., 1987; Graham & Mortimer, 1992; Scott et al., 2014; Wallace, 1974); see Section 2.3.2. As such, the principal assumption of this case study is that the Alpine Schist sample "1.AS", is the direct protolith to the Mataketake Pegmatite sample

(1(B)MP). Analyses of petrological, mineralogical, and geochemical variation between the pegmatite and its protolith is done with the objective of constraining the processes that led to melting, the conditions for melting, the composition of melt produced, and the subsequent implications for metal enrichment. Through applying recent work on melting and metal enrichment, such as Koopmans et al. (2023) and Kunz et al. (2022), we hope to further constrain the mechanisms that contribute to the formation of economic pegmatite deposits, which remain relatively poorly understood. This natural case study may be a useful complement to other experimental and modelled approaches.

1.5 Thesis Aims

At the highest level, this research intends to inform on the processes behind the formation of the Mataketake Pegmatites, then observe the extent of metal enrichment within the pegmatite and link the two to further understand the means for metal enrichment in context of recent literature. We endeavour to this through the following objectives:

- 1) We aim to provide detailed in-situ petrological descriptions on the Mataketake Pegmatites, and the Alpine Schists (from lower-greenschist through to lower-amphibolite/upper-greenschist facies). The principal aim is to provide contextual factors in the formation of the melt protoliths (Alpine Schist) and to analyse mineralogical relationships, textures, structural fabrics and microstructures to gain insights into the metamorphic history of the region that may implicate our later geochemical observations. Furthermore, there are a lack of “detailed and quantitative” petrological descriptions on the Mataketake Range Alpine Schists and Pegmatites (Beyssac et al., 2016), and consequently we will add to the few petrological descriptions to further petrographic knowledge within this region. See Chapter 4.
- 2) We aim to build on this contextual knowledge to better comprehend melt production, through major- and trace-element geochemical analyses of key phases: micas and feldspar. See Chapter 5 and 6.
- 3) We aim to use recorded mineral geochemistry to facilitate mass-balance modelling, using feldspar mineral-melt partition coefficients after Nielsen et al. (2017), and partition coefficients from other literature. Additionally, we aim to incorporate the empirical geothermometer of Henry et al. (2005) to constrain biotite formation temperatures within the Alpine Schist and Mataketake Pegmatites. We employ these methods with the objective of informing on melt reactions, mechanisms and processes. See Chapter 5 and 6.
- 4) We aim to evaluate our results in context of Koopmans et al. (2023) and Kunz et al. (2022), discussing the requirement for a Li-enriched protolith, multiple stages of melting, and the importance of micaceous melting, particularly biotite. See Chapter 6.
- 5) Finally, we aim to provide interpretations of melting types, conditions and composition in relation to other studies, such as: Briggs and Cottle (2018), Beyssac et al. (2016), Batt et al. (1999), and Wallace (1974).

1.7 Why the South Island, New Zealand?

New Zealand's South Island is an excellent natural laboratory for case studies on a variety of geological themes: fluid mobility, thermal regimes, metamorphism, elemental mobility, deformation processes, and mineral resources. The Alpine Orogen is young and relatively simple, with a well-studied history that allows for easier constraints on tectonics, deformation processes and fault structure.

The isolated pegmatites within the Mataketa Range provide opportunity for research into the very onset of partial melting, possibly informing on processes that contribute to melt formation, and melt enrichment/depletion. A key advantage of the pegmatites in South Island New Zealand, is that they represent a terrane dominated by (probable) fluid-induced melting, that has not been later 'destroyed' by dehydration melting of hydrous phases. This advantage is outlined in the work of Rubatto et al. (2009) for their study on the Central Alps (Europe). With pegmatites representing a significant portion of economic metal deposits, including Li, Cs, Ta, Be, Nb, Y, Sn, and F, they manifest an important area for geological research. Understanding the key drivers of pegmatite enrichment is of growing importance in an increasingly protectionist geopolitical theatre, with energy/resource security at the top of many political agendas.

Finally, the hinterlands of orogenic belts commonly accommodate economic pegmatite deposits (Bradley & McCauley, 2013; Bradley et al., 2017), and therefore pegmatites within the convergent Alpine Orogeny represent an opportunity for understanding pegmatite formation and the driving factors for pegmatite enrichment/depletion. Why are the Mataketa Pegmatites not enriched in elements such as lithium?

1.8 Thesis Structure

Chapter 2

We provide a high-level overview of New Zealand's geological foundations, which is informed from other literature. The breakup of Gondwana is described, and the associated geological processes that produced the proto-sediments for the Alpine Schists analysed in this study. We then detail the metamorphism that produced the Alpine Schists and the concomitant orogenies that have produced the structures within the South Island, the fabrics of the observed rocks, the micro-structures recorded in petrographic analyses, and finally the convergence that produced the Alpine Fault and uplifted the Southern Alps to their current topography. A summary of petrological observations of the Alpine Schist facies from other literature is then followed by an introduction of the Mataketa Pegmatites. Their location and occurrence is detailed. Previous thoughts on their formation are outlined. Prior petrographic descriptions are summarised, giving context to later petrographic analyses within this study.

Chapter 3

The methods used to carry out the case study approach are detailed here. Their reasoning, limitations and uncertainty are outlined.

Chapter 4

In this section, we detail petrographic observations for each of the specimens analysed. Starting with the lowest grade Alpine Schist facies, through to the upper-greenschist/lower-amphibolite facies Alpine Schists. We then note the petrology of the Mataketake Pegmatites, before providing a summary of key textural and mineralogical observations.

Chapter 5

Here we outline and compare the recorded mineral geochemistry of analysed plagioclase, biotite, and muscovite within the Alpine Schist and Mataketake Pegmatite. We also provide these results in context with other studies. We also compare mineralogical abundances between the protolith and the pegmatite. Trends within both major and trace elements are identified. A short section on cores, rims, and matrix grains is included.

Chapter 6

We discuss the significance of our observations from Chapters 4 and 5 in relation to the formation of the Mataketake Pegmatites. In addition to the implications of the basic geochemistry, we include secondary analyses through the manipulation of mineral geochemistry data to shed light on melting processes, which are vital for metal enrichment. This is done via: 1) the empirical geothermometer of Henry et al. (2005), which uses the relationship between biotite Ti contents and temperature to constrain the latter, 2) calculated whole rock concentrations of Sr, Rb and Ba, as well as normative Ab-An-Or to add to previous literature on the formation of the Mataketake Pegmatites (Briggs & Cottle, 2018), 3) mass-balance modelling of major elements K, Fe and Mg, 4) modelling of trace element melt compositions using the partition coefficients from the literature, mass-balance modelling is then completed with calculated melt trace element contents, and 5) Lithium melt composition is then modelled using muscovite and biotite mineral-melt partition coefficients from Icenhower and London (1995) and Koopmans et al. (2023). The limitations to these processes are outlined throughout this section. We then synthesise and critically evaluate the implications of this study for the melt reactions and processes that produced the Mataketake Pegmatites. This is given in context of other relevant literature. Finally, we then link this to metal enrichment and discuss the reasoning why the Mataketake Pegmatites are not enriched in Li, Sn and other metals. We particularly focus on the implications of this study for Li enrichment, following recent work of Koopmans et al. (2023) and Kunz et al. (2022).

Chapter 7

This section provides a conclusive overview of the significance of this study. We break this down into three sections: 1) what this study means for the Mataketake Region, 2) the impact of this study on understanding of metal enrichment in low temperature, partial melting pegmatite systems, and 3) areas for further research.

2 GEOLOGICAL SETTING

2.1 Geological Background of New Zealand

A combination of extensional and compressional tectonics has defined much of the complex history of New Zealand. The tectonic development has been driven by the dynamics of the breakup of Gondwana and subsequent plate boundary evolution. In the South Island, this history is expressed through the transpressional Alpine Fault, which has formed the Southern Alps.

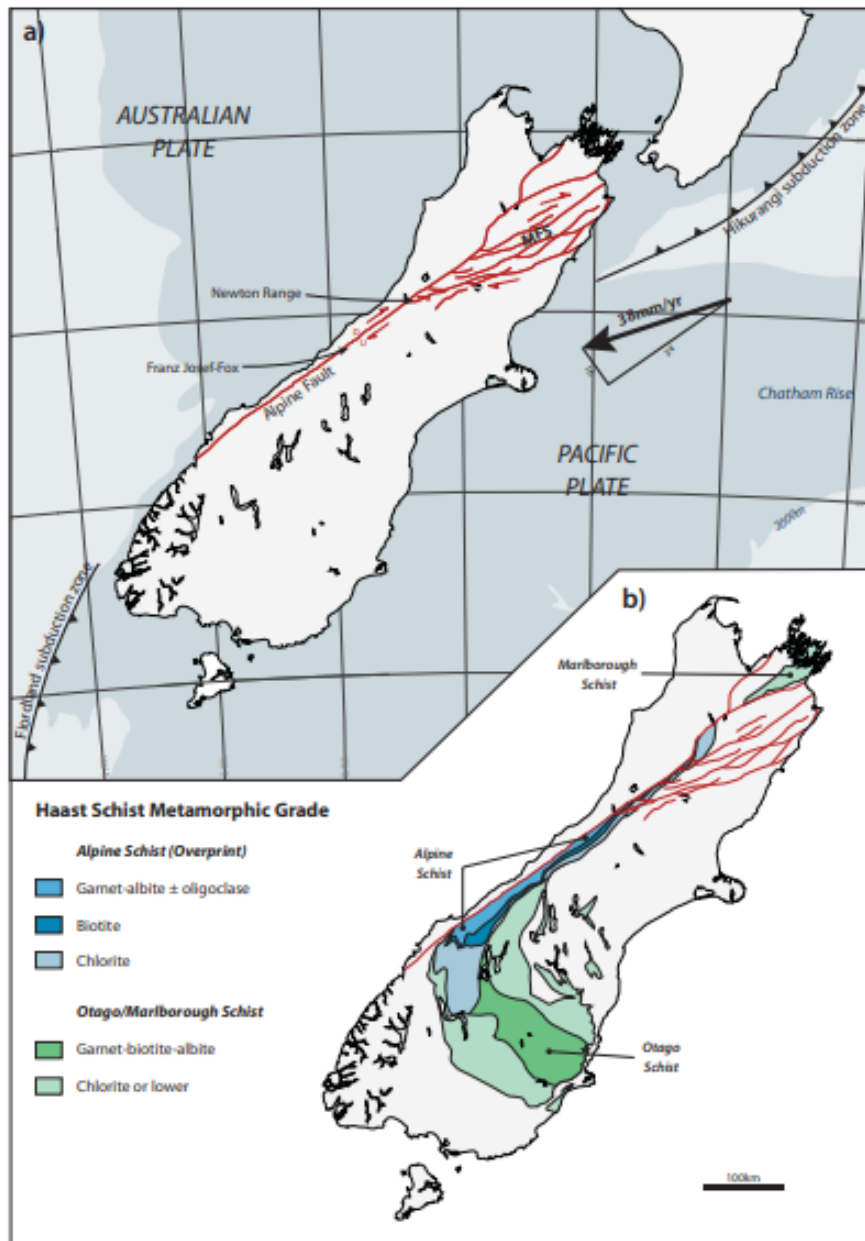
2.1.1 Tectonics and Regional Setting

New Zealand is situated in the southwest Pacific Ocean on the border of the Australian and Pacific Plates. The greater New Zealand region of Zealandia consists of continental crust encompassing basement schists, greywackes and granitoids (Mortimer, 2004).

Prior to the Late Cretaceous, New Zealand linked to Australia and Antarctica; forming a portion of Gondwana. Throughout the Cambrian to Early Cretaceous, volcanic and intrusive igneous activity, (e.g., that associated with oceanic arcs (Gray & Foster, 2004; Robertson et al., 2019)), subsequent erosion, and deposition (e.g., within accretionary wedge/backarc basin settings (Coombs et al., 1976; Gray & Foster, 2004)), occurred along the southern plate boundaries of the Gondwana continent, and produced the basement geologies that underly modern New Zealand (Mortimer, 2004; Mortimer et al., 1999). At a regional scale, the varied geology of South Island is grouped into the Western and Eastern Provinces, separated by the Median Tectonic Zone ((Mortimer et al., 1999) and references therein). The latter is most relevant to this thesis.

Tectonic extension occurred in the Late Cretaceous (~85Ma (Mortimer, 2004)), and the consequent break-up of Gondwana is evidenced through occurrences of lithological comparisons of the Western Province of South Island (New Zealand), and Australia, Northern Victoria Land and Antarctica (Menzies, 2012; Mortimer et al., 1999). Extension resulted in the thinning of the continental crust, forming rift basins such as the Great South Basin and Canterbury Basin (Barrier et al., 2021; King, 2000). Following the initial fragmentation of Gondwana, Zealandia remained relatively tectonically quiescent during the Late Cretaceous – Early Cenozoic; with a dispersed zone of deformation up to 200km wide at ~45Ma (Sutherland, 1995, 1999).

A



B

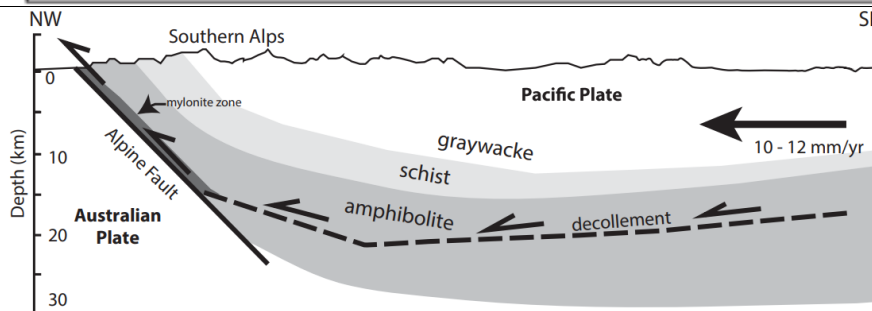


Figure 2.1: **A)** (Murphy, 2010) – **a)** tectonic setting of New Zealand's South Island. Arrow illustrates vector for modern plate motion. MFS = Marlborough fault system (Northeast of our study region). Dark blue shading depicts <2000m bathymetric contour. **b)** Map showing Haast Schists (Alpine and Otago Schists) and Marlborough Schist locations. Samples in this study span the Otago Schist and Alpine Schist. Shading indicates metamorphic grade. **B)** From Briggs and Cottle (2018) – depicting a schematic cross section across South Island, showing metamorphic progression from distal to proximal relative to the Alpine Fault.

In the Oligocene, the tectonic picture changed significantly as an increasing proportion of motion became margin-parallel at ~25Ma, resulting in the genesis of the Alpine Fault (Cooper et al., 1987; Sutherland, 1995). This proto-Alpine Fault system remained predominantly strike-slip until the late Miocene, when more convergent-dominated motion between the Pacific and Australian plates began (Cande & Stock, 2004; Sutherland, 1995; Walcott, 1998). The relationship at this boundary evolved as a major oblique-slip transform fault throughout the Miocene, and transformed into a dextral-reverse structure in the late Miocene, uplifting the Southern Alps (Cande & Stock, 2004; Murphy, 2010; Sutherland, 1995; Walcott, 1998). Although both strike-slip and compressional forces shaped the South Island of New Zealand, it was the latter that dominated the formation and uplift of the Southern Alps.

2.1.2 The Southern Alps; Background and Structure

The Alpine Fault and the Southern Alps are the backbone of the South Island of New Zealand. Basement rocks of South Island comprise Cambrian to Early Cretaceous lithologies formed along the southern boundary of the Gondwana plate (Mortimer et al., 1999). Three regional batholiths and nine volcano-sedimentary terranes underprint the basement rocks, which consist of three metamorphic belts (Mortimer, 2004).

The oblique-dextral Alpine Fault trends NE (055° strike) for ~850km along its strike, from southwest Fiordland up to its northernmost point near Marlborough (Norris & Cooper, 2001). The Alpine Fault is a transpressional fault that spans the South Island; presently the dominant motion of this fault is dextral strike slip, at a rate of 39mm/yr (Craw et al., 2002). The Southern Alps attain uplift rates up to 12mm/yr near Franz Josef-Fox Glacier region, with rates reducing to 6-8mm/yr to the north and south (Norris & Cooper, 2001; Walcott, 1998; Yetton & Nobes, 1998). In the central section, the Alpine Fault accommodates dextral slip at 27 ± 5 mm/yr (Little et al., 2005; Norris & Cooper, 2001; Williams et al., 2018). Uplift rates are limited by elevated erosion rates, owing to steep topography and intense rainfall (Walcott, 1998). The convergence associated with the current tectonic regime has only developed within the last ~10Ma (Batt et al., 1999; Norris et al., 1990; Sutherland, 1995, 1996). At ~5Ma a period of rapid exhumation led to a perturbed geothermal gradient and exposed higher-grade metamorphic rocks of the Alpine ‘Schist’ group (Batt et al., 1999). To the northeast, the Marlborough Fault System marks the transition from transform faulting and continental convergence of the Alpine Fault, to the Hikurangi margin to the north, where oblique subduction of Pacific crust occurs (Barnes et al., 1998; Collett et al., 2019).

The Alpine Schist dips steeply on the eastern side of the fault. In the central section, dip is estimated at ~45° (Stern et al., 2007; Williams et al., 2018), though it may reach up to ~60° elsewhere (Little et al., 2005), before flattening at depth. The Alpine Fault is segmented at a <10km scale, into deeply dipping, E-W-striking faults, which intersect gently dipping thrust components that strike NE-SW

(Barth et al., 2012; Langridge et al., 2014; Norris & Cooper, 1995, 2007; Simpson et al., 1994; Upton et al., 2018; Williams et al., 2018). Having undergone a metamorphic regime under a “normal” geothermal gradient, the metamorphosed stratum have been subsequently tilted and uplifted (Figure 4 in (Norris et al., 1990)). Rocks from as deep as 30km have been exhumed, with deeper rocks being the most intensely metamorphosed (Grapes, 1995). At ~20-30km depth a low-angle decollement is thought to separate the lower crust from the mid/upper counterpart (Norris et al., 1990). Delamination of the Pacific Plate away from the lower crust facilitates tectonic uplift of the mid/upper crust along the Alpine Fault, accommodating shortening of the Pacific Plate, whilst enabling the formation of the root of the Southern Alps via crustal thickening (Grapes, 1995). This delamination also tilts and “thrusts up the fault ramp” (Little et al., 2005; Murphy, 2010; Norris et al., 1990).

Within the Alpine Schist, retrogression of metamorphic intensity occurs with increasing distance from the fault. There is clear Barrovian facies continuation from garnet-oligoclase amphibolites, to garnet-biotite greenschist, to biotite-zone greenschists, to chlorite zone greenschists within the Haast Schists. As shown in Figures 2.1 & 2.2, the upper-greenschist/amphibolite facies lie proximal to the fault, along with a 1-km-wide mylonite overprint adjacent to the fault (Little et al., 2002; Norris & Cooper, 2003). Dominant foliation is oblique to the Alpine Fault.

2.2 Metamorphism in South Island, New Zealand

The South Island can be divided into the Eastern and Western Provinces, with the Median Tectonic Zone bisecting the two (Figure 2.2). The MTZ is an ancient terrane boundary, which formed during the accretion of Western Province and Eastern Province to Gondwana during the Mesozoic (reference). The Alpine Fault generally follows parallel to the MTZ and overprints the older suture. The Eastern Province is most relevant to this study, and can be separated into several terranes:

- Brook Street Terrane; a remnant root of a Permian intra-oceanic arc that existed along the Gondwana margin, consisting predominantly of ultra-mafic gabbros, diorites and volcanoclastic rocks intermixed with sedimentary sequences (Gray & Foster, 2004; Robertson et al., 2019).
- Murihiku & Maitai Terranes; closely associated. Murihiku is composed of Triassic-Jurassic sedimentary rocks, with lesser volcanoclastic rocks, principally derived from volcanic arcs, indicative of deposition in a forearc basin (Gray & Foster, 2004; Menzies, 2012). Sedimentary and volcanic rocks of the Maitai Terrane are older, deposited in the Permian to Early Triassic in a subduction-related forearc/accretionary wedge along the Gondwana margin (Robertson et al., 2019). The Maitai basin uncomfortably overlies the Dun-Mountain Ophiolite Belt (Campbell & Owen, 2003; Landis, 1974; Robertson et al., 2019).
- Dun-Mountain Ophiolite Belt: Permian ophiolite mélange, comprised of serpentinised ultra-mafic and mafic lithologies with a sedimentary cover. Interpreted as remnant section of

oceanic crust from a backarc basin along the Gondwana margin (Coombs et al., 1976; Robertson et al., 2019).

- Caples Terrane; accretionary wedge of Permian-Triassic age formed along Gondwana margin, dominated by metasedimentary rocks (particularly metagreywacke & argillite) (Adams et al., 1998; Robertson et al., 2019). Erosion of contemporary volcanic sources provided the sediments (Adams et al., 1998; Adams et al., 2009).
- Waipapa Terrane; composed of “monotonous” turbidite sequences, manifested as fine greywackes/siltstones, with occasional mudstones, cherts and volcanoclastics (Adams et al., 2017). More generally, the Waipapa Terrane formed as part of an accretionary wedge on Gondwana’s eastern Australian margin from the Permian to Early Cretaceous (Adams et al., 1998; Black et al., 1993). Petrographic and geochemical evidence points to a volcanic source (Black et al., 1993; Robertson et al., 2019).
- Torlesse Terrane; a composite subduction complex, comprised of turbiditic quartzofeldspathic sandstones, greywackes, and argillites (Gray & Foster, 2004; Menzies, 2012). The Torlesse Terrane contains the Rakaia Terrane (older Torlesse), Kaweka Terrane and the Pahau Terrane (younger Torlesse) (from west to east) (Robertson et al., 2019), and is of Permian to Early Cretaceous age (Mortimer, 2004).
- Haast Schists; metamorphosed equivalents of the Torlesse Terrane that are divided into the Otago and Alpine Schists.

The metamorphic regime in the Southern Alps was established in two stages (Grapes & Watanabe, 1992). Firstly, the Rangitata orogeny, responsible for uplift during the Jurassic/Cretaceous; this likely extended across the entirety of the accretionary wedge (Adams et al., 1985; Grapes, 1995; Sheppard et al., 1975). Uplift of 3-20km occurred between ~190-80Ma, at rates of 0.1-0.3m/m.y (Adams et al., 1985; Adams & Gabites, 1985; Grapes, 1995; Kamp et al., 1989; Tippett & Kamp, 1993).

Secondly, a concentrated rapid uplift (>5km/Ma) known as the Kaikoura Orogeny, led to the formation of the Southern Alps (Grapes & Watanabe, 1992; Kamp et al., 1989). Localised motion associated with the Kaikoura Orogeny within the Mount Tapuae-o-Uneku region possibly started ~25Ma in the Late Oligocene-Miocene (Collett et al., 2019; Cooper et al., 1987; Sutherland, 1995). Exhumation has become more widespread since, with Apatite Helium chronometers across the Marlborough Fault System (northeast South Island) from Collett et al. (2019) resetting at <10Ma (majority of data <5Ma). This coincides with the ages obtained for the thrust component of the transpressional slip at 5-10Ma (Batt et al., 1999; Cande & Stock, 2004; Sutherland, 1995, 1996; Toy et al., 2010). This most recent thrust component is responsible for rapid uplift and exhumation, producing a perturbed geothermal gradient, and exposing the multiple geologies of the hanging wall (Adams & Gabites, 1985; Batt et al., 1999; Collett et al., 2019; Cooper et al., 1987; Grapes, 1995; Grapes & Watanabe, 1992; King, 2000; Menzies, 2012; Toy et al., 2010).

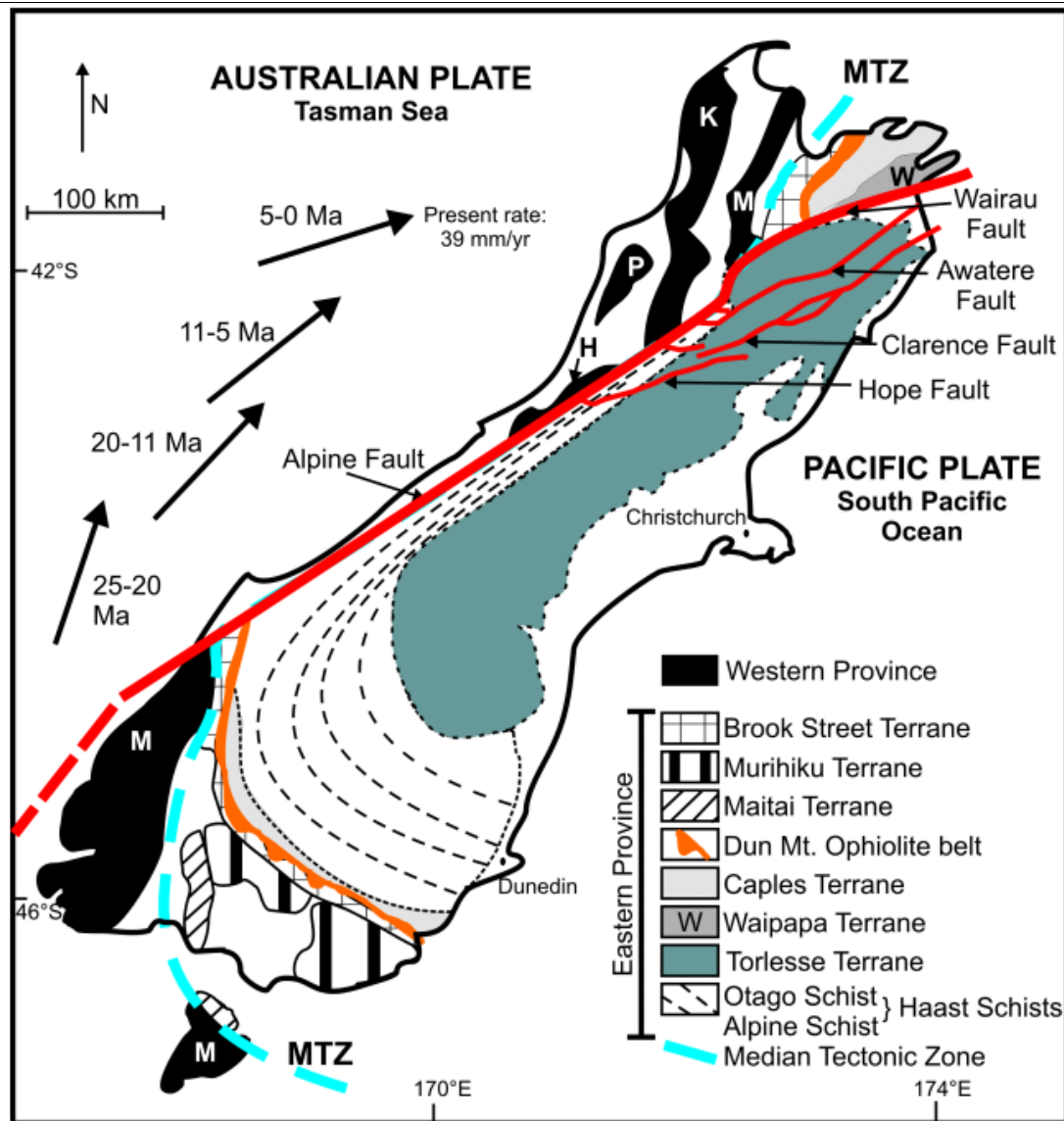


Figure 2.2: From Menzies (2012) – building on identification of Haast Schist and Marlborough Schist in Figure 2.1, this shows a simplified geological map of key metamorphic terranes outlined at start of Section 2.2. H = Hononu Batholith, K = Karamaea Batholith, M = Median Batholith, P = Paparoa Batholith. Arrows indicate relative plate motions in past 25Ma.

2.2.1 Torlesse Terrane, Haast Schists and the Alpine Hanging Wall

Pertinent to this study, the Alpine Hanging Wall is dominated by two lithological groups: the Torlesse Terrane and the Haast Schists (Figure 2.2). Summarised above, the Torlesse Terrane is an extensive, subduction-related accretionary complex consisting of stratified, yet structurally complex, quartzofeldspathic sandstones (greywackes) and mudstones (Roser & Korsch, 1999). Sourced from the Gondwana supercontinent, these sediments were transported via large river systems, and subsequently deposited off the eastern edge of southern Gondwana as greywacke-dominated turbidite sequences (Adams et al., 1998; Bradshaw, 1989; Mackinnon, 1983; Mortimer, 2004; Mortimer et al., 1999). Dating of detrital zircon and muscovite suggest I-type calc-alkaline granitoids dating to 230-

270Ma as the primary source of the Torlesse Terrane, with lesser constituents dating to 420-440Ma and 500-550Ma (Adams & Kelley, 1998; Ireland, 1992; Pitcairn, 2004). Age, composition, and volume constraints indicate the most probable origin of these sediments was the New England Orogen (northeast Australia) (Adams & Kelley, 1998; Pitcairn, 2004).

Metamorphosed equivalents of the Torlesse Terrane are the Haast Schists. The Haast Schists are comprised of Mesozoic metasediments that are subdivided into the Otago Schist and the Alpine Schist. The Alpine Schist resided at depth for a longer period than the Otago Schist and was uplifted more recently (Cooper & Palin, 2018; Ring et al., 2019). Metamorphism of the Torlesse terrane and Otago region initiated ~200Ma, in the Jurassic (Adams et al., 1985; Adams & Graham, 1997; Beyssac et al., 2016; Pitcairn, 2004). Metamorphic intensity is inversely related to Rb-Sr whole rock isochron ages, which span 200-120Ma; with early burial metamorphism at 200Ma, followed by regional metamorphism (Adams et al., 1985; Adams & Graham, 1997). During the Rangitata Orogeny (~142-99Ma), and into the Late Cretaceous (>80Ma), the eastern terranes were subjected to collision, accretion, uplift, and erosion, which were simultaneous with continued metamorphism of the Otago Schist (Fleming, 1969; Gray & Foster, 2004; Pitcairn, 2004). K-Ar and Ar-Ar dating of micas estimates peak metamorphism as Jurassic in age (Adams et al., 1985; Gray & Foster, 2004; Little et al., 1999). Mortimer (2000) estimate peak metamorphism of the Otago Schist at 350-400°C and 8-10kbar using (Ca-Mn) garnet-biotite geothermometer, and a white mica geobarometer.

The Alpine Schist has a prolonged tectonic history dating back to the Mesozoic (Ring et al., 2019). Deposition of protolithic Torlesse sediments continued up until the cessation of subduction along this frontier of Gondwana at ~105Ma, with detrital zircon of the Alpine Schist dating up until ~108Ma (Briggs & Cottle, 2018; Cooper & Palin, 2018). Several dating methodologies have been applied to the Alpine Schist, providing a range of timings for metamorphic growths. 5 zones of garnet growth within Vry et al. (2004) suggest multiple stages of metamorphism: 1) a Sm-Nd age of 97.8 ± 8.1 Ma for the garnet core, 2) 86.2 ± 0.2 Ma for Lu-Hf dating of stage 2, 3) Lu-Hf dating of 86.3 ± 0.2 Ma for overgrowth zone 3, 4) zone 4 dates to 12 ± 37 Ma through Sm-Nd dating, and 5) the garnet rim growth during recent thrusting ~5-6Ma. Other dates obtained for metamorphic growths within the Alpine Schist are set out in Table 2.1.

Geochronologic Method	Reference	Age (Ma)	Region
Lu-Hf Garnet	(Briggs & Cottle, 2018; Vry et al., 2004)	97.3 ± 0.3 to 75.4 ± 1.3	Southern Alpine Schist
Sm-Nd Isochron	(Mortimer & Cooper, 2004)	100 ± 12	Southern Alpine Schist
U-Pb Monazite	(Scott et al., 2015)	82.9 ± 2.3 , 82.6 ± 1.0	Fox Glacier
Lu-Hf Garnet	(Briggs et al., 2018)	79.9 ± 2.3	Hare Mare Creek
U-Pb Zircon Rims	(Cooper & Ireland, 2015; Cooper & Ireland, 2013; Cooper & Palin, 2018; Mortimer & Cooper, 2004)	72 to 64	Pounami ultramafic belt and Mataketake Region
Sm-Nd & Lu-Hf Garnet	(Vry et al., 2004)	97.8 ± 8.1 to ~ 5 (Multiple stages)	Mac's Creek, Arahura River, Tatare Stream, Whataroa River, Waikukpa, Moeraki River

Table 2.1: Geochronological indicators for the Alpine Schist.

The Haast Schists are principally comprised of quartzofeldspathic psammitic and pelitic schists, which contain lesser metabasic horizons (Pitcairn, 2004). A classic Barrovian facies progression occurs within this belt; from un-metamorphosed greywackes on the rims of the schist belt at its lowest grade, with progressively increasing metamorphic grade to the west, through to amphibolite facies rocks adjacent to the Alpine Fault in the mid-West of South Island, New Zealand (Grapes, 1995; Grapes & Watanabe, 1992; Murphy, 2010) (Figures 2.1 & 2.2). In the past 5-10 Ma, rapid uplift has exposed higher-grade rocks, including those of amphibolite facies, during the Kaikoura Orogeny that produced the Southern Alps. Upper-greenschist to amphibolite facies rocks were exhumed from as deep as ~ 30 km in the crust, at which point the Alpine Fault reaches a decollement (Murphy, 2010; Norris et al., 1990).

Late Cenozoic and continued tectonic forces have resulted in a mylonitic overprint of the Alpine Schist to the east of the Alpine fault, strengthening schistose foliation which formed during Mesozoic metamorphism (Briggs & Cottle, 2018; Little et al., 2002; Norris & Cooper, 2003). Ring et al. (2019) constrain the mylonitisation of amphibolite-facies rocks of the Alpine Schist to 13.1 ± 4.3 Ma to 8.9 ± 3.2 Ma using Rb-Sr muscovite isochron ages.

Metamorphic conditions for the Alpine Schist vary by location. In the Franz Josef-Fox Glacier area (Figure 6.4), thermobarometric data for K-feldspar zone schists suggested P-T conditions of 420-620°C and 5.2-9.2 kbars (Grapes, 1995). Peak metamorphic conditions in this region, using garnet-biotite thermometers and garnet-plagioclase Ca-partitioning barometers, are confined to 600-700°C and 9.2-10 kbar (Grapes, 1995; Grapes & Watanabe, 1992). Ti-in-biotite thermometry has also been applied to mylonitic rocks from Harold, Gaunt Creek, Hare Mare Creek, and Little Man River (Figure 1 within (Toy et al., 2010)), which have corroborated the high temperatures above (Toy et al., 2010).

Toy et al. (2010) also note that the Ti-in-biotite thermometer indicates biotite reequilibration for much of the experienced temperature range during exhumation; with syn-mylonitic temperatures as low as 300°C. Raman spectroscopy of carbonaceous material (RSCM) data from Beyssac et al. (2016) record peak metamorphic temperatures of 650-700°C proximal to the Alpine Fault (including mylonitic samples), through to <330°C at a distance of 15-20km southeast. This study contained a range of samples: from the Copland River, in the northeast, to the Haast river in the southwest. This is probably the most accurate estimate of temperature, with the irreversible nature of graphitisation resulting in RSCM thermometry being insensitive to retrograde equilibration/alteration (Beyssac et al., 2002).

2.2.1.1 Alpine Schist Petrology

Chlorite Zone to Biotite Zone Greenschist Facies

Comprised of quartz, albite, chlorite, muscovite, epidote, carbonaceous material, magnetite/hematite, pyrite ± calcite and stilpnomelane (Pitcairn, 2004). Grapes and Watanabe (1994) additionally report titanite, tourmaline, and apatite, with no observed magnetite/hematite, pyrite, or calcite. Wallace (1974) observes plagioclase as the dominant phase, which attain complex twins, and consistent lamellae of deformation-twins. Quartz and feldspar-rich layers contrast with darker chlorite, epidote and muscovite-rich layers forming lighter and darker segregations (Murphy, 2010; Pitcairn, 2004; Wallace, 1974). These segregations are often folded and/or deformed into ellipsoids of quartz and feldspar which bisect the darker layers (Pitcairn, 2004). It is this segregation that gives the Alpine Schist its schistosity. Pitcairn (2004) note the 'lath' habit of chlorite and muscovite in the darker domains.

The biotite zone schists are very similar, with the obvious increase in biotite content to the detriment of chlorite (Grapes & Watanabe, 1994; Pitcairn, 2004). Pitcairn (2004) identifies the same mineralogy as the chlorite-zone, but with the addition of sphene, and no stilpnomelane. Whereas, Murphy (2010) reports the following additional phases: amphibolite, ilmenite, and tourmaline in the Alpine Schist of Newton Range, evidencing spatial heterogeneity within the schist. Pervasive segregation into aforementioned lighter and darker domains has occurred (Pitcairn, 2004).

Garnet Zone Greenschist Facies

Development of garnet, and more intense biotite formation (at the expense of chlorite), differentiates these samples from biotite zone greenschist facies. Observed mineralogy is: quartz, plagioclase, biotite, muscovite, garnet, epidote, graphite, hematite, and pyrite ± calcite (Pitcairn, 2004). Grapes and Watanabe (1994) note the presence of albite and oligoclase, as well as chlorite, ilmenite, tourmaline, apatite, graphite and pyrrhotite. Unlike Pitcairn (2004) and Grapes and Watanabe (1994), Wallace (1974) notes K-feldspar (orthoclase) as a minor constituent. The mesoscopic structure remains similar, with lighter and darker segregations of quartz-feldspar, and mica-garnet (Wallace,

1974). Garnets occur as porphyroblasts, often attaining a “snowball” texture, indicating synkinematic formation to initial deformation during metamorphism (Wallace, 1974). Wallace (1974) notes radiating chlorite grains at some garnet boundaries, indicating retrogressive alteration. Micas are abundant (Wallace, 1974), although Pitcairn (2004) records a much lesser abundance of muscovite. Muscovite and biotite are noted to show retrogressive textures (Wallace, 1974). These occur as a phengitic corona for muscovite, while radiating chlorite and fine rutile exsolve along biotite cleavage (Wallace, 1974). Epidote and chlorite are rare in these samples (Pitcairn, 2004). Plagioclase:quartz ratio increases concomitantly with metamorphic grade (Pitcairn, 2004).

Garnet-Oligoclase to K-Feldspar Zone Amphibolite Facies

Oligoclase zone rocks have the following mineralogy: quartz, plagioclase (oligoclase), biotite, garnet, graphite, magnetite (& hematite), pyrite $\pm$ calcite (Pitcairn, 2004). Grapes and Watanabe (1994) additionally note andesine, white mica, ilmenite, tourmaline, apatite, and pyrrhotite. Wallace (1974) notes a “simple mineralogy of plagioclase and hornblende” and observes other phases as accessories. Chamberlain et al. (1995) observe key mineralogy as plagioclase, hornblende, biotite, garnet, epidote, calcite, titanite and rutile. Pitcairn (2004) notes that extensive development of amphibole is only located in metabasic lithologies, which are interlayered with the much more abundant quartzofeldspathic schists. Wallace additionally records epidote, sphene, rutile and “occasional metamorphic pyroxene” (Wallace, 1974). Disparity in observations can be attributed to spatial heterogeneity within the Alpine Schist, with Wallace (1974) stating hornblende as the major component, and Pitcairn (2004) recording biotite and plagioclase as the most abundant phases. Micas are large, reaching lengths of 3mm. Texturally, the samples are still segregated into quartz-plagioclase (lighter), and biotite, muscovite and garnet (darker) layers (Pitcairn, 2004). Lamellae of plagioclase and quartz outline the mesoscopic structure (Wallace, 1974). Idioblastic garnet porphyroblasts achieve diameters up to 1cm and are dominated by almandine compositions (Wallace, 1974). Alteration to oxide and sulphide phases is “considerable”, with sulphides forming trails correlated to biotite (Pitcairn, 2004). K-feldspar zone is texturally similar, with the introduction of K-feldspar (Grapes & Watanabe, 1994).

2.3 The Mataketake Pegmatites

2.3.1 Location

In the Mataketake Range, between the Haast River and Doughboy Creek, and within 2-3km southeast of the Alpine Fault, lies a ~5km wide zone where pegmatite dikes and sills extend at least 27km along strike (Batt et al., 1999; Briggs & Cottle, 2018; Chamberlain et al., 1995; Wallace, 1974)(Figures 2.3 & 6.4). Within the Southern Alps, these pegmatites, along with a series of lamprophyric dykes, are the only exposed intrusive rocks (Batt et al., 1999; Cooper et al., 1987). Exposure of these pegmatites is most pronounced in the Mataketake Range, although Briggs and Cottle (2018) note Mount Kinnaird

hosts the highest observed density of these intrusions. Adjacent to the Alpine Fault, the mylonite zone hosts these pegmatites, producing progressively altered and deformed occurrences (Briggs & Cottle, 2018; Norris & Cooper, 2003).

Generally, pegmatite intrusions lie concordant to schistosity and measure 0.15-30m thick, with some up to 40m thick (Briggs & Cottle, 2018; Wallace, 1974; Wellman, 1955). Occasional dikes cross-cut sills (Briggs & Cottle, 2018). Intrusions commonly form tapered pods, with some reaching lengths up to 250m (Wallace, 1974). In the Mount Kinnaird region, an interconnected network of pegmatites form pods that taper along strike to the north and south (Briggs et al., 2018). Field relationships indicate injection at similar P-T conditions to metamorphism of the Alpine Schist, with no evidence of baked margins nor alteration of xenoliths (Wallace, 1974). Pegmatite-Alpine Schist boundaries are often “patchy” and “irregular”, appearing gradational in outcrops (Briggs & Cottle, 2018). Quartz veins occur through much of the Mataketake Region, and intrusion-parallel quartz veins are located within many sills (Briggs & Cottle, 2018).

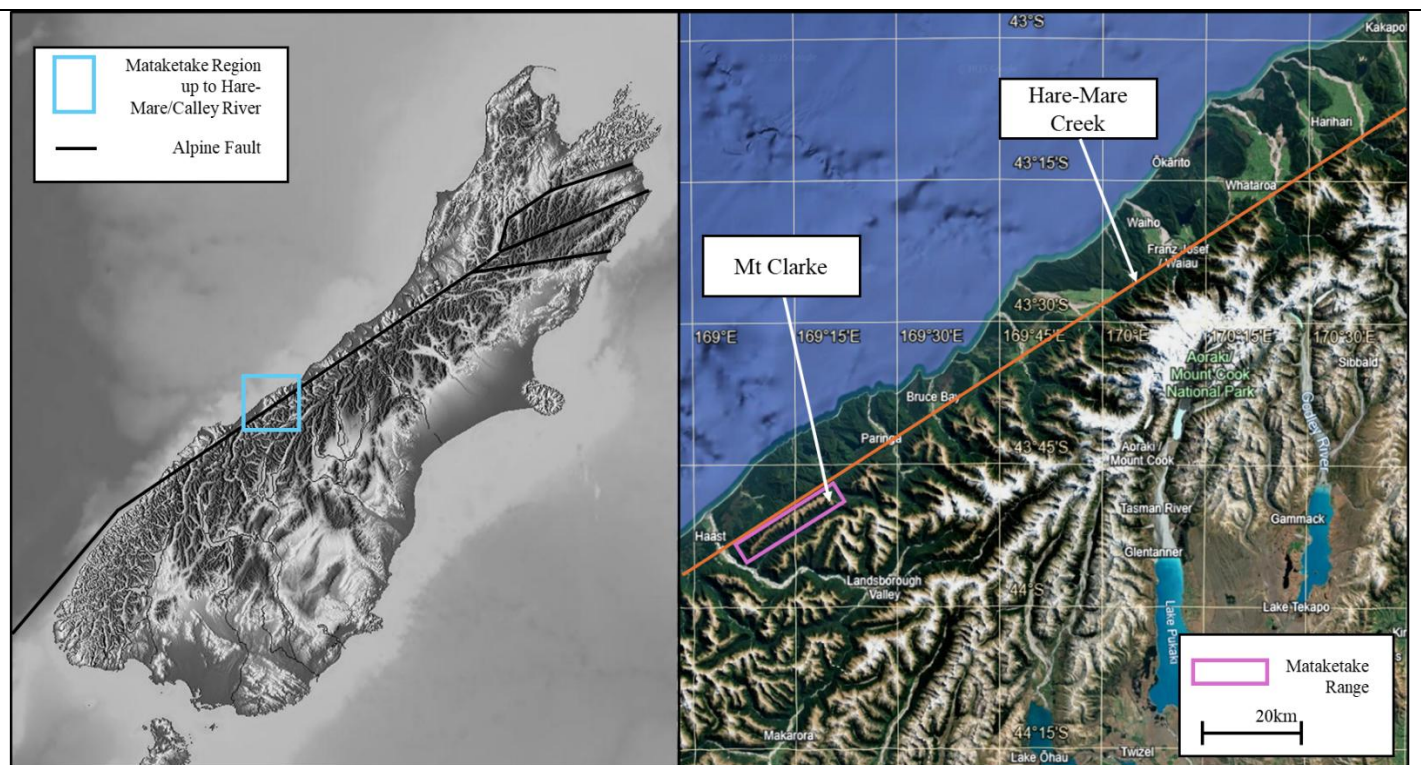


Figure 2.3: Location map showing the principal study region within the wider context of the South Island. This thesis is mainly focussed in the regions spanning the Mataketake Range up to the Hare-Mare Creek. Although other samples are included to contextualise the study.

2.3.2 Formation

Field observations and petrology indicate the pegmatites formed from partial melting of the Alpine Schist country rock (Wallace, 1974). $^{87}\text{Sr}/^{86}\text{Sr}$ studies of the Otago Schists and pegmatites corroborate

this interpretation. $^{87}\text{Sr}/^{86}\text{Sr}$ of the pegmatites was calculated at 0.7053 at 68Ma (Aronson, 1965), and K-feldspar-muscovite two-mineral isochrons for the pegmatites produce model $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of 0.7060 and 0.7059 (Batt et al., 1999). Whereas $^{87}\text{Sr}/^{86}\text{Sr}$ of the Otago Schist are recorded between 0.7061 and 0.7098 (Aronson, 1965; Graham & Mortimer, 1992). Briggs and Cottle (2018) record $\varepsilon_{\text{Hf}}(t)$ signatures between 0 to +11 within zircons. This is consistent with the Alpine Schist, which has whole-rock $\varepsilon_{\text{Hf}}(t)$ values of -3 to +9 (Briggs & Cottle, 2018; Briggs et al., 2018). Scott et al. (2014) examined xenoliths from mantle underlying the South Island, which varied in $^{87}\text{Sr}/^{86}\text{Sr}$ from ~ 0.7025 , to ~ 0.7043 . More appropriately, xenoliths from West Otago (hosted in carbonatitic-lamprophyric Alpine Dike Swarm (proximal to Mataketake Region) (Cooper et al., 1987)), attained $^{87}\text{Sr}/^{86}\text{Sr} < 0.7030$ (Scott et al., 2014). As such, the underlying mantle can be discounted as the pegmatite source due to lesser radiogenic Sr.

Various methods have been used to date the Mataketake Pegmatites. Chamberlain et al. (1995) date the pegmatites to $68 \pm 2.6\text{Ma}$ and $67.9 \pm 2.5\text{Ma}$ using U-Pb monazite and zircon ages. Batt et al. (1999) use multiple methods to date the thermochronology of the pegmatites to yield cooling histories: 1) U-Pb ages of zircon give formation estimates of $69.8 \pm 2.2\text{Ma}$, $81.5 \pm 1.4\text{Ma}$, $67.3 \pm 2.1\text{Ma}$ and $74.4 \pm 2.2\text{Ma}$, 2) Rb-Sr dating of K-feldspar and muscovite between at $71.1 \pm 0.7\text{Ma}$ and $64.4 \pm 2.3\text{Ma}$, and an apparent Rb-Sr biotite age of $11.3 \pm 0.5\text{Ma}$, 3) K-Ar and ^{40}Ar - ^{39}Ar age determinations give a separate range of $3.64 \pm 0.05\text{Ma}$ to $26.0 \pm 0.3\text{Ma}$. This variation in determined ages communicates a dynamic cooling history, with a largely uniform thermochronological history. However, a marked decrease in cooling rate at 5Ma followed by intense cooling is thought to mark the onset of significant exhumation (Batt et al., 1999). This coincides with the Alpine regime, from strike-slip faulting to oblique convergence that formed the Southern Alps. U-Th/Pb dating of zircon, xenotime, and monazite by Briggs and Cottle (2018) suggest an age range from $\sim 80\text{Ma}$ to 50Ma for pegmatite emplacement. This period of $\sim 30\text{m.y}$ for melt generation is much longer than previously thought.

2.3.2.1 Melting of the Alpine Schist

Studies on the anatexis processes that produced the peraluminous granitic pegmatites are limited. Peak metamorphic temperatures are thought to have occurred simultaneously, or immediately preceded, partial melting (Batt et al., 1999; Mortimer & Cooper, 2004; Scott et al., 2015). Wallace (1974) uses experimentally calibrated reactions and mineral assemblages (petrology) to suggest P-T conditions in the Mataketake Range between 4.7-7.3kb and 625°C - 680°C , which Wallace indicates as “similar” conditions to the partial melting of Alpine Schist. Elsewhere, RSCM thermometry indicates temperatures may have reached $\sim 700^{\circ}\text{C}$ (Beyssac et al., 2016).

Briggs and Cottle (2018) utilise accessory mineral petrochronology, specifically monazite, xenotime, and zircon, to define a broad time range of anatexis, from around 85-50Ma. They analyse 12

pegmatite samples, spanning the entire geographic and geochemical extent of the (observed) region. They state that this time zone represents primary crystallisation, remelting of existing pegmatites and fluid-assisted recrystallisation (Briggs & Cottle, 2018). Garnet growth initiated between ~100-110Ma and persisted to around 70Ma (Briggs & Cottle, 2018; Mortimer & Cooper, 2004; Vry et al., 2004). The oldest monazite dates for pegmatites are ~85Ma, with many samples attaining ages that align with the latter end of garnet growth (~80Ma). Consequently, monazite and zircon dates indicate that melting initiated whilst metamorphic garnet growth was coming to an end.

Rb/Sr and Ba concentrations can be used to infer H₂O-present or H₂O-absent muscovite melting (Inger & Harris, 1993; Patiño Douce & Harris, 1998; Simons et al., 2016; Weinberg & Hasalová, 2015). Elevated Rb and depleted Sr in mica contradicts the enriched Sr and limited Rb in plagioclase (Inger & Harris, 1993; Weinberg & Hasalová, 2015). Rb, Ba and Sr are useful for modelling processes as they partition into feldspars and micas, rather than accessory phases (Simons et al., 2016). Consequently, mica-dehydration reactions produce high Rb/Sr ratios relative to water-fluxed melting. Ba inclusion in this system is attributed to its compatibility in K-feldspar, and thus it measures its involvement in reactions (Zeng et al., 2005). Briggs and Cottle (2018) therefore analyse whole-rock compositions of the Mataketake Pegmatites to infer melting reactions. These indicate melting of the Alpine Schist via H₂O-present muscovite-breakdown (Figure 2.3) (Briggs & Cottle, 2018; Inger & Harris, 1993). Two analysed pegmatite samples within Briggs and Cottle (2018), seem to indicate H₂O-absent dehydration melting (Figure 2.3).

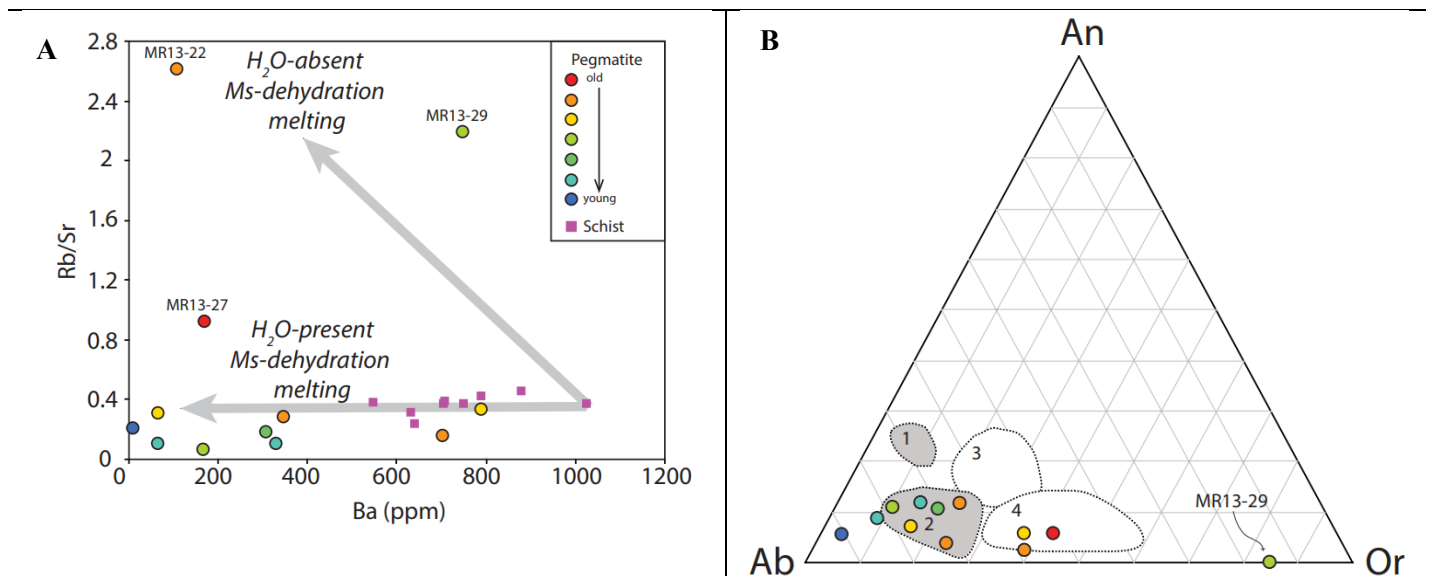


Figure 2.4: Figures taken from Briggs and Cottle (2018) **A**) Rb/Sr vs Ba for whole-rock analyses of 12 pegmatite samples from the South Island, New Zealand. (Briggs & Cottle, 2018) **B**) Briggs and Cottle (2018); An-Ab-Or normative ternary plot. Blobs show melting reactions from literature (shaded = water-present melting reactions), (non-shaded = dehydration melting reactions). “(1) H₂O-saturated melting of dacite/graywacke (Conrad et al., 1988), (2) H₂O-present melting of mica schist (Patiño Douce & Harris, 1998), (3) H₂O-understaurated melting of dacite/graywacke (Conrad et al., 1988), (4) dehydration melting of tonalite (Patiño Douce, 2005)” (Briggs & Cottle, 2018).

An-Ab-Or normative ternary plots can provide insight into varying source-rock compositions or differing water activity (Briggs & Cottle, 2018; Patiño Douce & Harris, 1998; Weinberg & Hasalová, 2015). At elevated water activity, melts are enriched in Ab and An, whilst depleted in Or (Briggs & Cottle, 2018; Weinberg & Hasalová, 2015). By applying this hypothesis under the assumption that melt source composition was homogenous, Briggs and Cottle (2018) infer that water-fluxed melting was dominant. They also suggest the possibility that H₂O-absent dehydration melting contributed to earlier melts, with MR13-29 (Figure 2.4) enriched in Or, along with older samples contained in the region '4'. The grey fields represent H₂O-present melting reactions, and the opposite for white fields. '1' & '3' represent H₂O-present and -absent melting of dacite and greywacke from Conrad et al. (1988). '2' covers compositions produced by water-present melting of mica schist (Patiño Douce & Harris, 1998). Finally, '4' displays compositions produced via dehydration melting of tonalite (Patiño Douce, 2005).

Briggs and Cottle (2018) conclude that partial melting occurred over a period of ~30m.y, initiating ~80Ma. The sustained anatectic period is better supported by semicontinuous melt generation via H₂O-fluxed melting, which aligns with whole-rock Rb/Sr vs Ba records and the An-Ab-Or ternary plot (Briggs & Cottle, 2018). Rubatto et al. (2009) communicate that melting in these scenarios can occur repeatedly (upon water influx) where the system lies above the wet-melting solidus, thus providing a mechanism for semicontinuous melt generation over 30m.y. Indication of H₂O-absent melting by Briggs and Cottle is limited to select samples (Figure 2.4) and is therefore tentative.

Both the Rb/Sr vs Ba, and the An-Ab-Or systems assume homogeneity within the melt protolith (Alpine Schist). However, heterogeneity is well documented within the Alpine Schist (Beyssac et al., 2016; Menzies, 2012; Mortimer et al., 1999; Murphy, 2010; Pitcairn, 2004; Wallace, 1974)(This study). Therefore, it is entirely possible that compositional variation in pegmatites may be due to varying melt source whole rock compositions. Additionally, the significance of whole-rock assemblages can be limited (McCarthy & Groves, 1979; Villaros & Pichavant, 2019). Therefore, further research on the origins of the Mataketake Pegmatites is beneficial.

2.3.3 Petrology of Mataketake Pegmatites

Key minerals are identified as quartz, plagioclase, K-feldspar, which occur as medium-coarse grains, as well as varying muscovite, biotite and garnet quantities (Briggs & Cottle, 2018). Wallace (1974) notes that “perthitic alkali feldspar is a major constituent”, of compositions ~Or₉₂₋₉₅. Batt et al. (1999) highlights quartz, muscovite and K-feldspar as the dominant phases. Tourmaline, apatite, zircon, monazite and xenotime occur as accessory phases (Briggs & Cottle, 2018; Chamberlain et al., 1995). The garnet-mica pegmatite contains disorientated books of massive muscovite and biotite porphyroblasts up to 60x25x12cm (Wallace, 1974). This is contradictory to the aligned foliation-parallel micas that occur in the pegmatites, which give the appearance of a weak fabric (Briggs &

Cottle, 2018). Post-crystallisation deformation is reflected through kinked books (Wallace, 1974), and within the Alpine fault mylonite zone, large mica fish, “extensive” subgrain quartz formation, and grain-size reduction visible in rims of feldspar augen all contribute to a protomylonitic texture (Briggs & Cottle, 2018). The prevalence of myrmekitic intergrowths and unzoned euhedral garnets of the almandine-spessartine variety are noted by Wallace (1974).

3 METHODOLOGY

3.1 Hand Specimen & Petrological Analyses

Samples (n=6) were collected by C.Menzies from the South Island of New Zealand in June 2023, with additional samples being sent by D.Craw. They comprised metamorphic rocks ranging from chlorite schists, through to biotite-garnet grade gneisses. 2 samples were pegmatites from the Mataketake Region. Hand specimen and petrological observations determined the lithology types, key features, and major mineralogy.

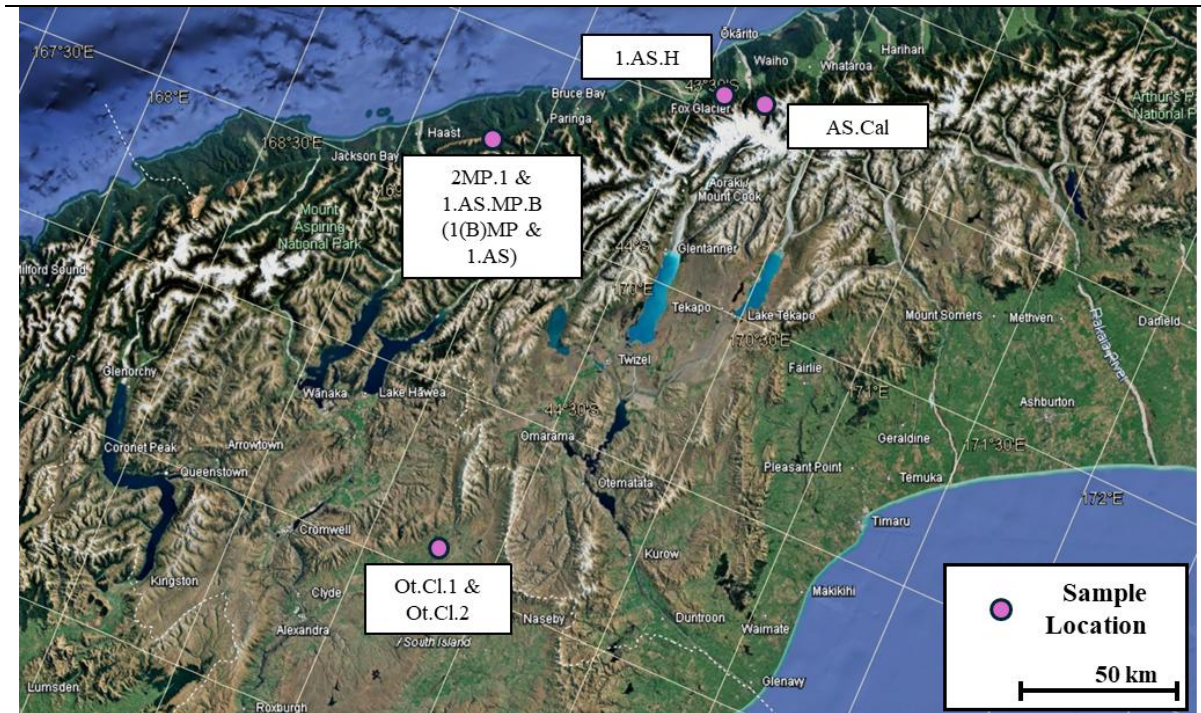


Figure 3.1: Map of the central portion of New Zealand's South Island, marking sample source locations (Underlying map from Google Earth). The 6 samples rock samples are: Otago chlorite schists (Ot.Cl.1 & Ot.Cl.2), Alpine Schist from the Callery Tributary (AS.Cal), Alpine Schist from Hare Mare Creek (1.AS.H), an Alpine Schist – Mataketake Pegmatite border hand specimen from Mount Clarke (1.AS.MP.B) and a Mataketake Pegmatite sample from Mount Clarke 2MP.1. Note that the border specimen (1.AS.MP.B) is divided into three thin section samples for analysis – 1.AS.H (covering the border of both the schist and pegmatite), 1.AS (the Alpine Schist section), and 1(B)MP (the pegmatite section).

Polished petrographic sections were prepared at the Department of Earth Sciences, Durham University, and included 80um 'thick' sections and 40um 'thin' sections. Polished sections were used for optical microscopy to determine key textural, structural, and mineralogical observations. Further detail on micro-textures, and major element compositions of key phases were determined through Scanning Electron Microscopy (SEM) of polished 'thick' sections.

3.2 SEM Analyses

3.2.1 Imaging

Back-scattered electron (BSE) imaging of samples was done using a Hitachi SU-70 high resolution analytical SEM in the GJ Russell Electron Microscopy Facility, Durham University. All SEM analyses, including imaging, were done using a Beam Working Distance of 15mm, with the Anode Lens positioned at 3, and the Objective Aperture positioned at 1. A voltage of 15.0kV was used, with Probe Current set to Medium.

Due to the fine-grained nature of many of the lesser-metamorphosed rocks, BSE-imaging was necessary to identify mineralogy, and textural relationships within the Chlorite Schists. More widely, BSE-imaging allowed for observation of micro-textures, compositional variations, and phase relationships.

3.2.2 Geochemical Analysis

The EDS detector was used for EDX analyses with Aztec 6.1 software. EDS analysis was done on 1.AS, 1(B)MP, the boundary between these two lithologies, and a separate pegmatite sample from the Mataketake Range (2MP.1).

EDX analyses were completed for accurate mineral identification and to quantify major-element composition. Key phases to analyse were muscovite, biotite, and plagioclase because they represent significant constituents of collected samples, and therefore exert notable control on bulk rock geochemistry. Furthermore, micas can host trace elements, particularly critical metals, in abundance and consequently play a vital role in trace element partitioning during crustal melting.

Quantification for major element data (O, Si, Na, Ca, Al, K, Fe, Mg, Ti), was done for areas >40x40um, as this was the slit-size of choice for Laser Inductively Coupled Mass Spectrometry (Laser ICP-MS). To obtain EDX analyses, the following Aztec Acquisition settings were used: Input 'SE', Speed at 45µs, Process Time at 4, Energy Range of 20keV and an Acquisition Time of 8s. A Process Time of 4 was chosen to provide sufficient energy resolution to distinguish overlapping elements, whilst maintaining Output Count Rate such that Dead Time was within optimal range (40-60%). The data from EDX analyses were also used as elemental internal standards, for Laser ICP-MS data that was later collected.

3.2.2.1 EDS Data Processing

Once Spectra had been acquired, the 'Confirm Elements' tab within Aztec enabled identification of existing elements. Identification of elements was based on the given uncertainty, (sigma value) for Aztec, and the knowledge of expected geochemistry within requisite phases.

Following data collection, analysis took place in Excel, where figures were plotted and statistical calculations completed (Appendices “Biotite Analysis.xlsx”, “Feldspar Analysis.xlsx”, “Muscovite Analysis.xlsx”). Matlab was used to draw up geochemical plots.

3.3 Geochemical mapping

Chemical Mapping was completed in Aztec, utilising the same SEM settings as in Section 3.2.

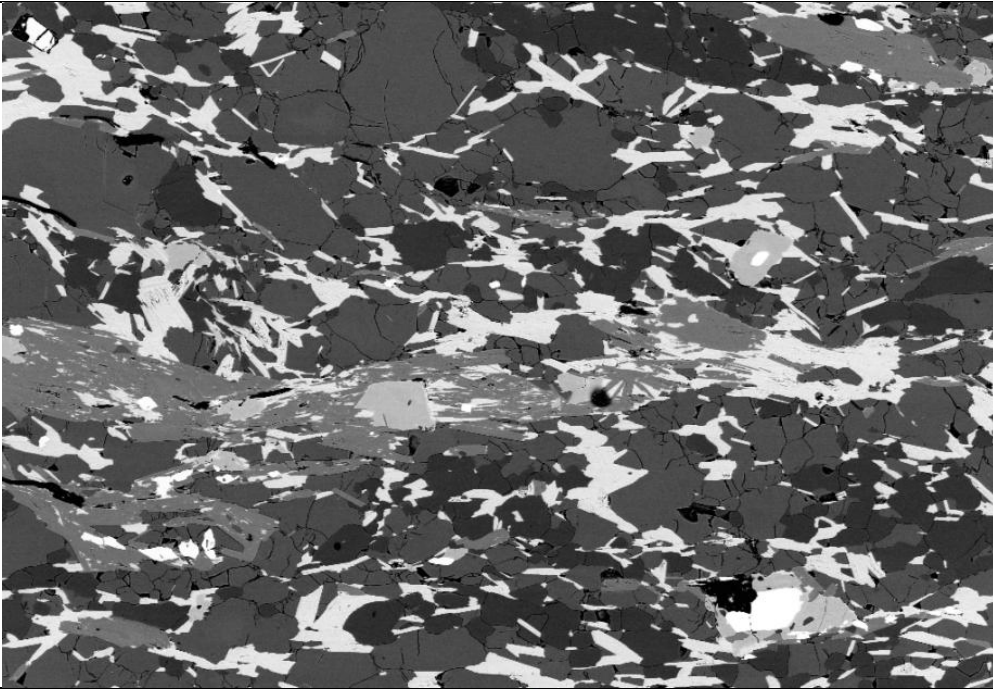
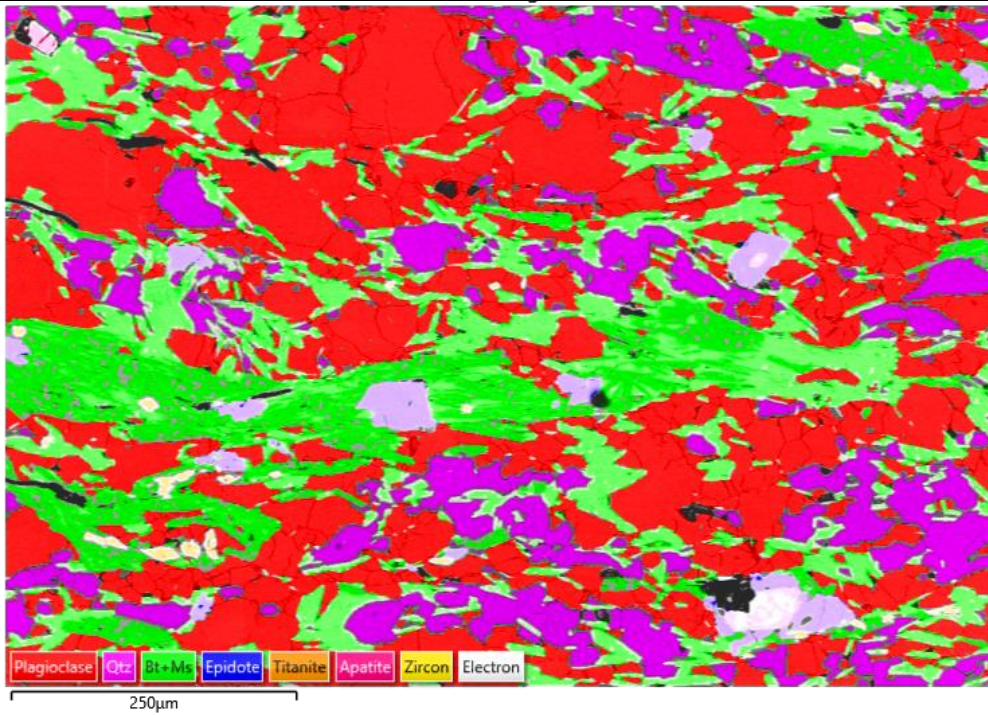
Electron Imaging was also completed for each map area, as this provided a visual comparison against chemical data. Once data were gathered, the numerous Site locations were montaged, to produce larger maps. This involved manual alignment of Site locations. Once chemical maps were montaged, phase maps were produced. A Binning Factor of 2 was used for the Trumap function. Within ‘Find Phases’, a Grouping Level of 0.5, and a Boundary Tolerance of 1.5 was used for all maps. These manual settings enabled more distinct grouping of phases, which was important due to the fine-grained nature of accessory phases and the micas. It is also meant that significant portions of the produced phase map were ‘Unassigned Pixels’. This introduced uncertainty in mineral quantification and affected finer, matrix-dominated phases to a greater extent, as these phases had a higher ratio of grain perimeter:area occupied, compared to porphyroblastic grains, which had less perimeter per area of geochemical map occupied. Geochemical mapping facilitated analyses of accessory phases, and the extent to which they persisted.

3.4 Compositional Quantification Using Aztec

The phase maps outlined in Section 3.3 were then used to quantify mineralogical compositions of the Alpine Schist (1.AS) and the Mataketake Pegmatite (1(B)MP). As the absolute size of phase maps varied, mineral quantification was done using the percentage of total pixels occupied by each phase, instead of averaging out the mineral quantity (%) for each map. There were 5 phase maps for 1.AS, covering 9,528,780 pixels, and 6 phase maps were used for 1(B)MP, covering 21,005,274 pixels. Pixel size remained constant for 1.AS at 0.84914 μ m, and for 1(B)MP at 0.97977 μ m, therefore a much larger area was mapped for 1(B)MP.

Although settings were manually adjusted to account for the fine-grained nature of certain grains, issues arose with the grouping of biotite and muscovite whilst phase mapping (Figure 3.2). This was due to their occurrence as fine-grained, sheared, anastomosing aggregates (Figure 3.2.A), (n.b., muscovite did also occur as discrete porphyroblasts). Aztec was unable to differentiate the similar compositions at the fine levels, and manual settings could not be changed without compromising the accuracy of other phases. To further differentiate mica grains, FIJI(ImageJ) software was used. ImageJ facilitated the isolation of micas using their specific grayscale threshold values. Due to the similar grayscale of biotite to other phases (titanite, apatite, zircon), muscovite was isolated, then ‘Despeckled’, to increase precision, and provide a percentage fraction for muscovite. This percentage

fraction was then subtracted from the combined biotite+muscovite fraction, to give requisite values for each mica. Pixel counts were then calculated from these values.

A**B**

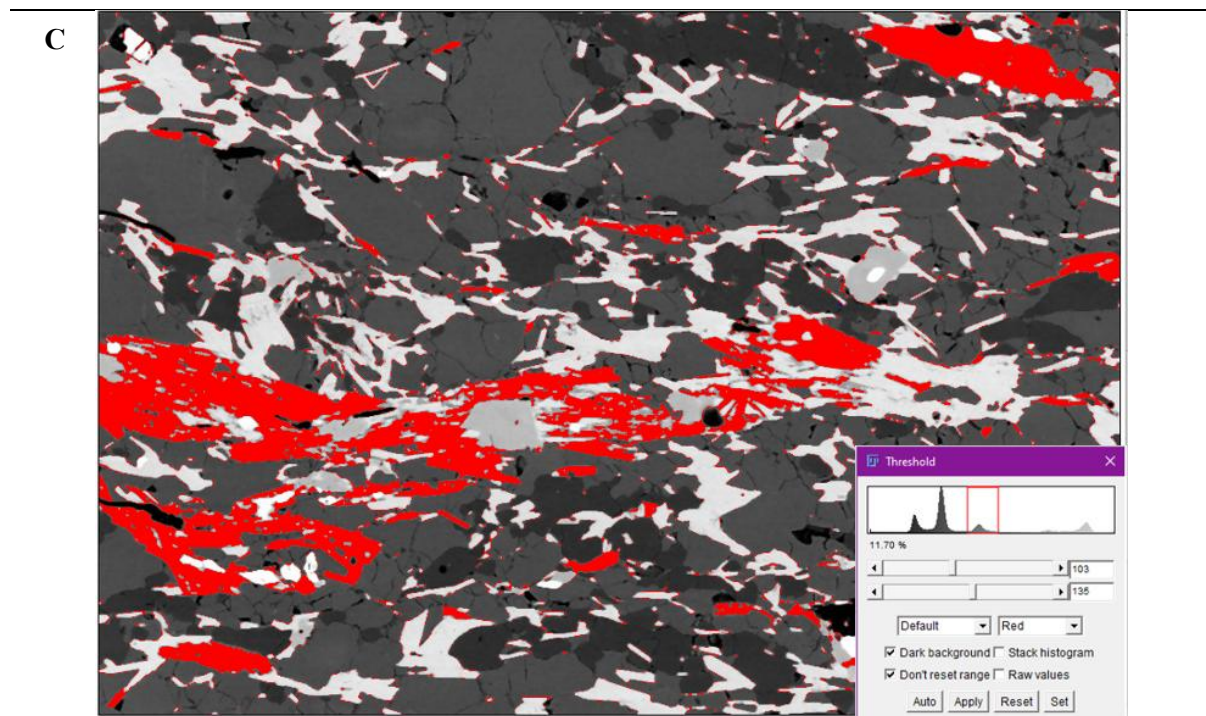


Figure 3.2: *A: Electron Image for Phase Map 3. Grayscale depends on signal intensity, corresponding to varying average atomic numbers, with strong signals producing bright areas. Black = no signal (holes), Dark Grey = Quartz, Medium Grey = Plagioclase, Medium-Light Grey = Muscovite, Light Grey = Epidote, Grey-White = Biotite, White = Titanite/Apatite/Zircon. B: Phase Map 3 from 1.AS. Note how the micas have been grouped into a single 'phase'. C: Isolated muscovite highlighted red. The confined range of threshold values is illustrated in the threshold distribution function. Muscovite comprises 11.70% area of this map.*

3.4.1 Geochemical Mapping Uncertainty

There are limitations to geochemical mapping, phase mapping and subsequent compositional quantification, some of which is unavoidable and difficult to quantify.

There are limitations associated with the texture of the analysed samples. The banded texture of 1.AS and even 1(B)MP can mean that the region analysed may skew results. For example, analysing a quartz-plagioclase dominated section, or a mica-enriched region will affect compositional abundances. Another example would be the analysis of a quartz vein, which will result in over-prediction of quartz quantities. To minimise the effects of this, multiple maps were completed for 1.AS and 1(B)MP, to cover a wide area of the thick section, and to gain a more holistic quantification of phase abundances. Other textural limitations are detailed in 2.4. Firstly, the inability for Aztec to distinguish between muscovite and biotite within fine-grained aggregates was mitigated using ImageJ to quantify mica abundances based of the grayscale threshold of muscovite. Secondly, the occurrence of garnet as discrete porphyroblasts, which are not ubiquitous in the thick section, may have resulted in a low quantification of garnet abundance.

The pixel size relative to grain size introduces uncertainty that disproportionately affects finer grains. For micaceous aggregated, much of this uncertainty has been mitigated through ImageJ. However,

more generally, the heterogenous nature of grain sizes results in uncertainty. This was limited through the manual selection of settings in phase mapping. Binning factor was increased to 2, so that noise was reduced, which aids in identification of smaller grains, and differentiates mineral compositions to a greater extent.

3.5 Laser ablation ICP-MS Analyses

Laser ablation ICP-MS was used to determine concentrations of trace elements using a Teledyne Cetac Analyte Excite+ laser ablation instrument. The laser is coupled to a Thermo Scientific iCAP-TQe mass spectrometer. The software used to upload sample locations was Chromium 2.4. Settings for the laser were: Flows: 0.5 LPM He within the cell and 0.3 LPM He added within the extraction arm, energy setpoint of 4.0mJ, a laser energy at 65% and a fluence of 4.47 J/cm², a pressure of 6050mbar, a voltage of 0.92kV, a repetition rate of 6Hz, and a burst count of 180 shots. For each phase and date, the trace elements analysed, and their requisite dwell times are displayed in Table 3.1.

Analyses of feldspars, biotites, and muscovites across the Alpine Schist (1.AS) and Mataketake Pegmatite (1(B)MP) were collected in batches of 8-10, with international standards (NIST610, NIST612, BHVO, BCR, and StHS) separating batches and to ensure the instrument is performing well. International standards NIST610 and NIST612 were also used at the beginning and end of each run.

3.5.1 Laser-ICP-MS Data Processing

Data from Laser ICP-MS were processed using Iolite 4; a data reduction program specifically designed to process MS data (Paton et al., 2011). Background counts were subtracted from the measured total using 'Baseline Subtract' within Iolite 4. International standard NIST610 was used as a primary reference material to calibrate data quantification. EDS data was used as the internal standard; Al was used for micas, and Ca was used for feldspars.

3.5.2 Laser Ablation ICP-MS Error/Uncertainty

For Laser ablation ICP-MS data, the uncertainty values were 2-Standard-Error output from Iolite. Limits of detection (LOD) were based off Longerich et al. (1996). Other uncertainties can arise due to isobaric interferences, where isotopes with similar mass:charge ratios interfere with one another. The use of a high-resolution MS and a manual selection of dwell times aims to mitigate this uncertainty. Precision and accuracy can be difficult to maximise during trace element analyses, particularly for complex, fine-grained textures, where larger laser spot sizes and higher dwell times are not feasible. Laser spot sizes were maximised at 40x40µm to improve precision. Other unavoidable uncertainties are ablation yield and laser-induced fractionation, whereby certain elements may be preferentially ablated, and material from deeper in the sample may have a longer time delay before reaching the MS.

Table 3.1: Trace elements analysed for each mineral, their dwell times (s), and the date of analyses.

Trace Element Analysed	Dwell Time (s)			
	22/04/24 Muscovites	22/04/24 + 23/04/24 Feldspars	03/07/24 Biotites	03/07/24 Feldspars
⁷ Li	0.01	0.05	0.02	0.05
²³ Na	na	0.001	0.001	0.001
²⁴ Mg	na	na	0.01	na
²⁵ Mg	na	0.01	0.01	0.01
²⁷ Al ,	0.001	0.001	0.001	0.001
²⁹ Si	0.01	na	0.01	na
⁴³ Ca	0.01	0.01	0.01	0.01
⁴⁴ Ca	0.01	na	0.01	na
⁴⁵ Sc	0.02	na	0.02	na
⁴⁸ Ti	0.05	na	na	na
⁴⁹ Ti	na	0.01	0.01	0.01
⁵¹ V	0.1	na	0.1	na
⁵² Cr	0.05	na	0.05	na
⁵⁵ Mn	0.01	0.01	0.02	0.01
⁵⁷ Fe	na	na	0.01	na
⁵⁹ Co	0.1	na	na	na
⁶⁶ Zn	0.01	0.05	0.01	0.05
⁶⁷ Zn	0.02	0.02	0.02	0.02
⁷¹ Ga	0.1	na	0.1	na
⁸⁵ Rb	0.01	0.05	0.02	0.05
⁸⁶ Sr	0.01	0.01	0.01	0.01
⁸⁸ Sr	0.02	0.02	0.02	0.02
⁸⁹ Y	0.02	0.02	0.02	0.02
⁹⁰ Zr	0.02	na	0.02	na
⁹³ Nb	0.1	na	0.1	na
¹¹⁸ Sn	na	na	0.1	na
¹³³ Cs	0.02	0.05	0.02	0.05
¹³⁷ Ba	0.01	0.02	0.01	0.02
¹³⁹ La	0.1	0.02	0.1	0.02
¹⁴⁰ Ce	0.1	0.02	na	0.02
¹⁴¹ Pr	0.02	0.02	na	0.02
¹⁵³ Eu	na	0.02	na	0.02
¹⁷² Yb	0.1	na	0.1	na
¹⁸² W	na	na	0.1	na
²⁰⁸ Pb	0.02	0.02	0.02	0.02

na=not analysed

3.6 Data Processing & Calculations

Major element data collected from SEM-EDS, and trace element data from Laser ICP-MS were used to calculate mineral stoichiometry to give atoms per unit formula (apfu) for muscovite and biotite following Deer et al. (2013). See Appendix files “Biotite Analysis”, “Feldspar Analysis”, and “Muscovite Analysis” for apfu calculations for this study. Plagioclase compositions (X_{An} and X_{Or}), were calculated in excel, please see the appendix file “Feldspar Analysis”.

After the work of Nielsen et al., (2017), trace element compositions of plagioclase were considered whilst accounting for X_{An} . Basic mass-balance modelling was done within the Sr, Ba and Pb system.

These elements were chosen as there were data available in Nielsen et al., (2017). Melt contents of Sr, Ba and Pb were calculated from plagioclase data, with Xan accounted for. The four principal phases (quartz, plagioclase, muscovite, and biotite) comprised >95% of both the Alpine Schist and the pegmatite, and therefore are assumed to have dominant control on trace element partitioning. Expressions were then set up for plagioclase, muscovite, and biotite. The role of quartz was assumed to be negligible in the partitioning of these elements. These expressions were then used to model different melt quantities of the four principal phases. This modelling was done whilst considering feasible melt reactions for the Mataketake Pegmatites. The empirical thermometer of Henry et al. (2005) utilised Ti-in-biotite to calculate biotite closure temperatures. Matlab was used to plot figures.

4 PETROLOGY

Samples were collected from the South Island of New Zealand by Dr.C.Menzies in the summer of 2023. Six samples were collected, reflecting increasing grades of regional metamorphism, from the chlorite schists of Callery, up to the biotite-garnet Hare-Mare Schists and amphibolite facies Alpine Schists, which have been shown to be the protolith for the final samples of Mataketake Pegmatites. Samples from the Mount Clarke area (Figure 3.1 (2MP.1 & 1.AS.H (1(B)MP, 1.AS))) were sourced from boulders close to outcrops. This is because outcrops were significantly weathered, whereas boulders were less altered and therefore were better for subsequent geochemical analysis. It is important to note that samples are not oriented, and therefore no kinematic information can be gained from them.

As outlined in Chapter 2, the progressive metamorphism expressed in the samples is characteristic of Barrovian facies metamorphism, which occurred during the Mesozoic (Adams et al., 1985; Adams & Graham, 1997; Beyssac et al., 2016; Pitcairn, 2004). Following the initial period of metamorphism, a second period of deformation occurred in the Cenozoic, during uplift of the Alpine Hanging Wall (Briggs & Cottle, 2018; Little et al., 2002; Murphy, 2010; Norris & Cooper, 2003; Norris et al., 1990). This has resulted in an overprint of deformation, which dominates the observed textures in the higher-grade Alpine Schists and Mataketake Pegmatites. The Alpine Schist comprises both the Otago Schist and Haast Schist, and forms part of the Torlesse Terrane.

In this chapter we describe observed mineralogy, texture and microstructures from collected samples. This provides context for later geochemical analyses. We then make preliminary interpretations, considering these observations in relation to previous petrography, before further building on these with geochemical observations, which are detailed in Chapter 5.

4.1 Alpine Schist; Chlorite-Zone/Lower-Greenschist Facies

Chlorite Schist (from the Callery Tributary) (AS.Cal (+bt))

Mineralogy: quartz (~50%), plagioclase (~10%), chlorite (20%), muscovite (10%), minor biotite and opaques (~10%) (apatite, Ti-Fe oxides, and carbonaceous phases). Hand specimen shows well segregated, alternating light-green-grey domains, dominated by quartz, albite and chlorite, and darker coloured streaks enriched in chlorite, muscovite, and opaques (apatite, Ti-Fe oxides, and carbonaceous material), as well as light coloured, quartz veins. The intrusive quartz veins, for example as seen on the left of Figure 4.1, are clear evidence for hydrothermal activity within the sample region. The fabric of the schist is apparent in hand specimen and is evidenced by the contrasting domains.



Figure 4.1: Chlorite Schist from the Callery Tributary, with intruding quartz veins.

Optical microscopy allows for clear observation of these varying domains. The lighter coloured domains are quartz dominated but contain copious albite and chlorite grains aligned with the paleo-fabric (Figure 4.2) and have lesser quantities of muscovite than darker domains. The lighter coloured domains also contain the occasional apatite, as well as other opaque phases. In contrast, within the darker veins, it is impossible to observe any grains in thick section. Primarily, this is most probably due to the alignment of muscovites and the thickness of the section, but also the increased abundance of opaque phases and the fine-grained nature. Segregations are generally unfolded (planar) in this sample, however the pervasive segregations occasionally form ellipsoids of quartz, albite and chlorite.

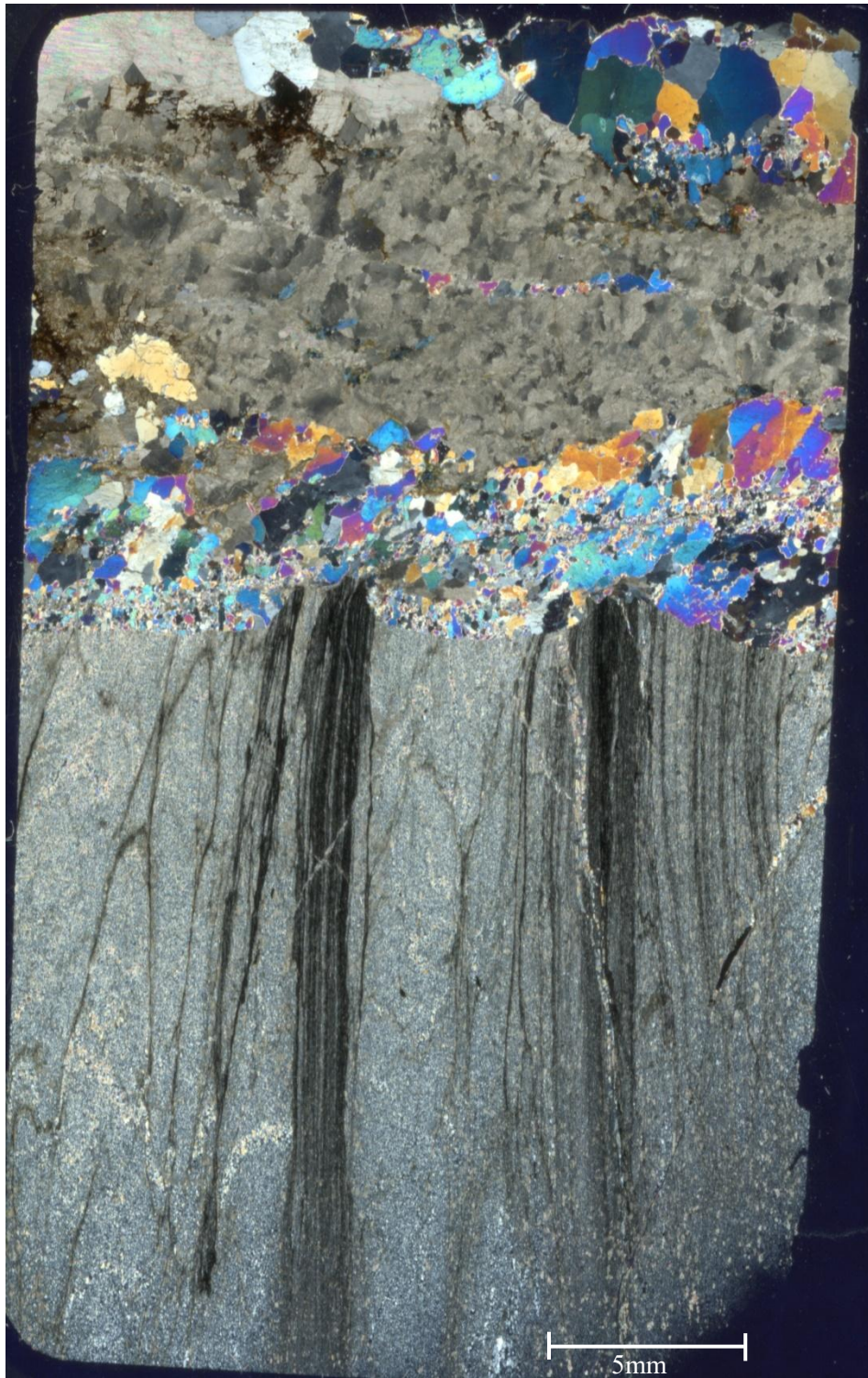


Figure 4.2: AS.Cal 80um Thick Section Scan. Quartz ribbons occur as swathes and coarse quartz + calcite vein crosses the top of the section. Quartz dominates the light-coloured domains, with albite and chlorite as well.

Otago Chlorite Schist (Ot.Cl.1 & Ot.Cl.2)

Mineralogy: quartz (~45%), plagioclase (~2%), chlorite (~20%), muscovite (~25%), and opaques (~8%): magnetite, haematite, apatite. Segregated domains of light-grey-green and darker greys (near black). Schistose fabric is highlighted by fissile nature of hand specimen. Lighter regions are dominated by quartz and albite, with some chlorite, which is aligned with the fabric. The contrasting darker regions are dominated by chlorite and muscovite. Coarser opaque phases, including magnetite, and apatite clearly contrast to the lighter quartz-dominated domains. Much of the lighter green/grey colours are overprinted by surface oxidation (likely oxidised haematite), which is clearly visible in Figure 4.3.

Segregations often appear folded, due to deformation. Ellipsoidal patches of the lighter quartzofeldspathic domains occur, with occasional laths of chlorite and muscovite. Quartz veins crosscut the schistosity, indicating later-stage fluid activity.



Figure 4.3: Ot.Cl.1 – Otago Chlorite Schist from the Manukerikia region. Showing lighter and darker coloured domains. Brown colour is likely derived from oxidation of Fe, which is contained in chlorite, and Fe-oxides.

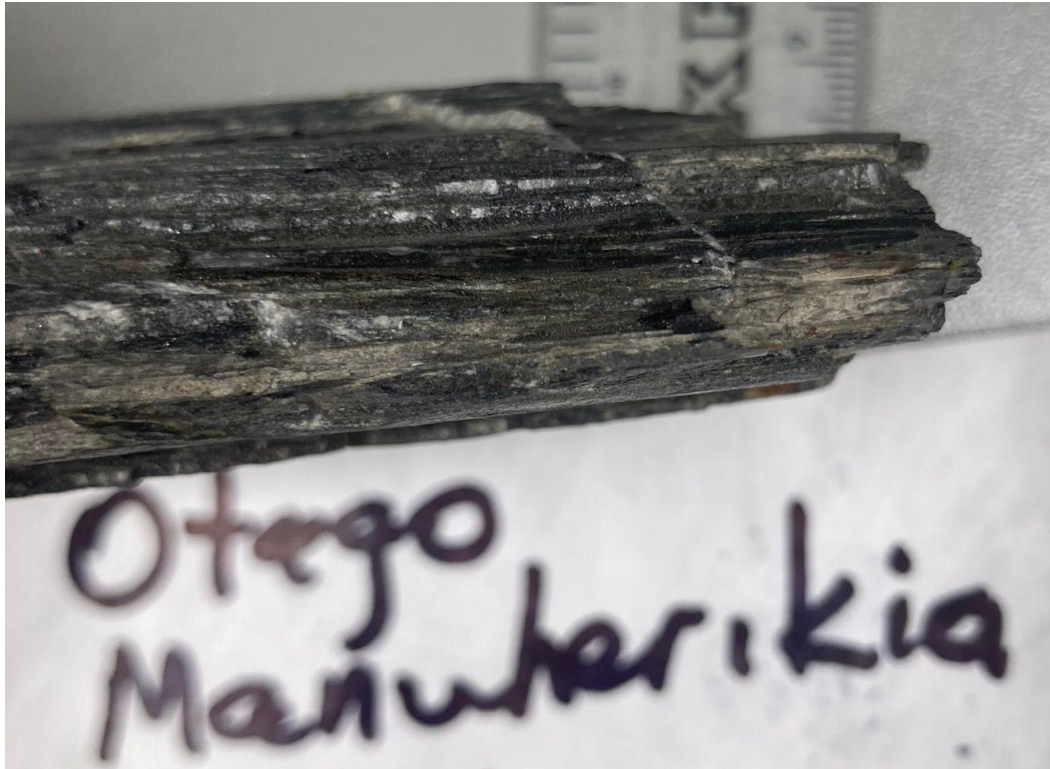


Figure 4.4: Ot.Cl.2 Alternative view to Figure 4.3, showing the layered structure, creating a reasonably fissile metamorphic rock. The dark coloured layers are muscovite dominated, and contribute to the platy structure.

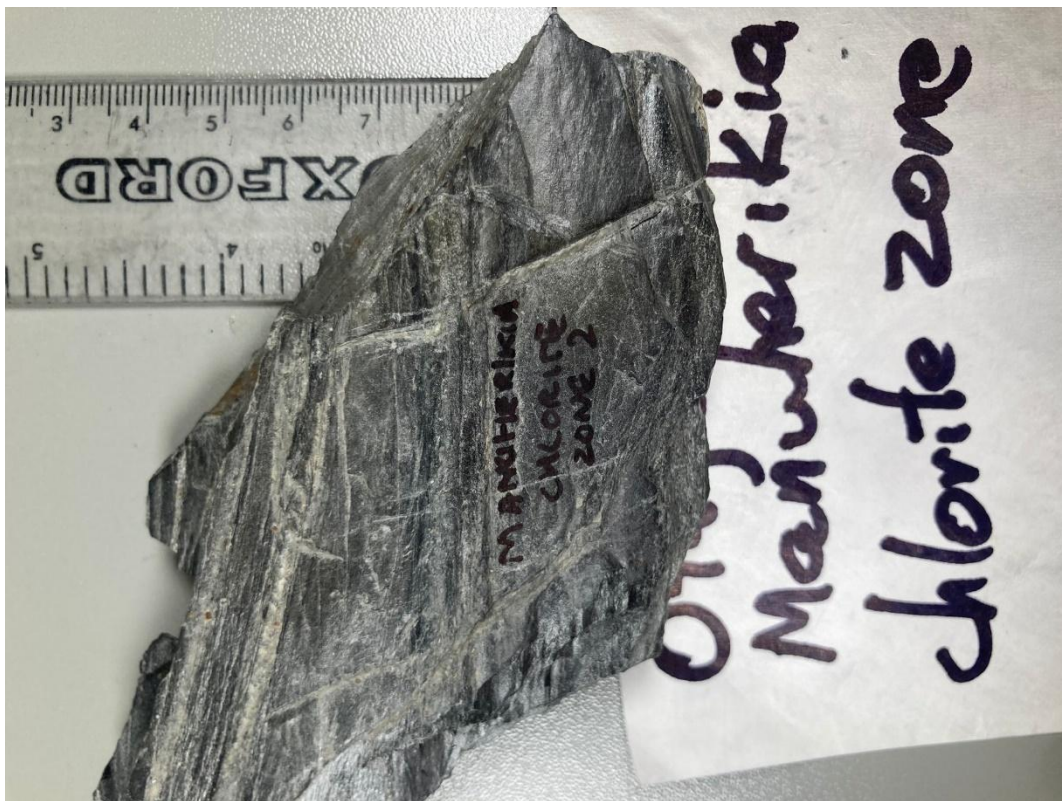


Figure 4.5: Ot.Cl.2 – the fissile, platy nature due to metamorphic alteration and alignment of mica minerals. Orthogonal view to Figure 4.3, looking at the surface of the fabric.

In thick section, much of the mineralogy is difficult to identify. The coarser, undulating, quartz veins stand out. Segregations are clear, with lighter regions dominated by quartz, with lesser albite and chlorite, contrasting to the chlorite and muscovite dominated darker regions. Within the lighter regions, occasional laths of chlorite and muscovite occur. The fine grain size of the darker regions makes petrological observation difficult.



Figure 4.6: Photomicrograph of Ot.Cl.2 PPL (Left) and XPL (Right). Quartz vein cross cuts the segregations of quartzofeldspathic, chlorite domains (light), and chlorite, muscovite, and epidote rich regions (Dark)

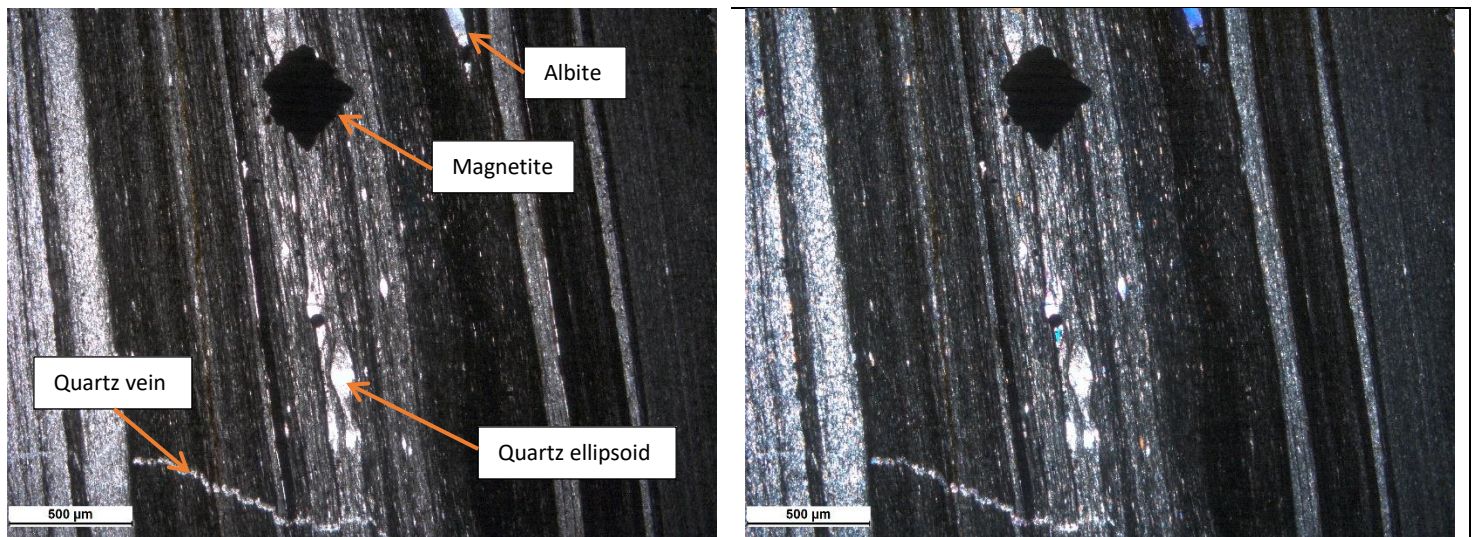


Figure 4.7: Photomicrograph of Ot.Cl.2 in PPL (left) and XPL (right). Clear segregations of light and dark, reflecting mineralogical changes. Ellipsoids of quartz and albite, which may possibly be porphyroblasts with pressure shadows ('wings'), and laths of chlorite and muscovite occur in the lighter domains. A larger opaque grain, likely magnetite is observed in the middle of a lighter segregation.

SEM observations allowed for clear observation of the darker domains, and showed the platy mica crystals, observed along their long axis, with chlorite, epidote, and opaque phases also present (Figure 4.8). Magnetite, apatite, and haematite comprise most opaques. Some opaque phases are notably

coarser than the rest of the mineralogy, such as pyrite (Figure 4.9). The following images highlight key textures and mineralogy (Figures 4.8-4.11). The varying domains (Figure 4.8) likely derive from the original sedimentary protolith and are ubiquitous through the Haast Schist through the entire metamorphic progression. Figures 4.9 & 4.11 display porphyroblasts formed through continuous metamorphic growth. Figure 4.11 shows a partially replaced muscovite porphyroblast with tapering pressure shadows.

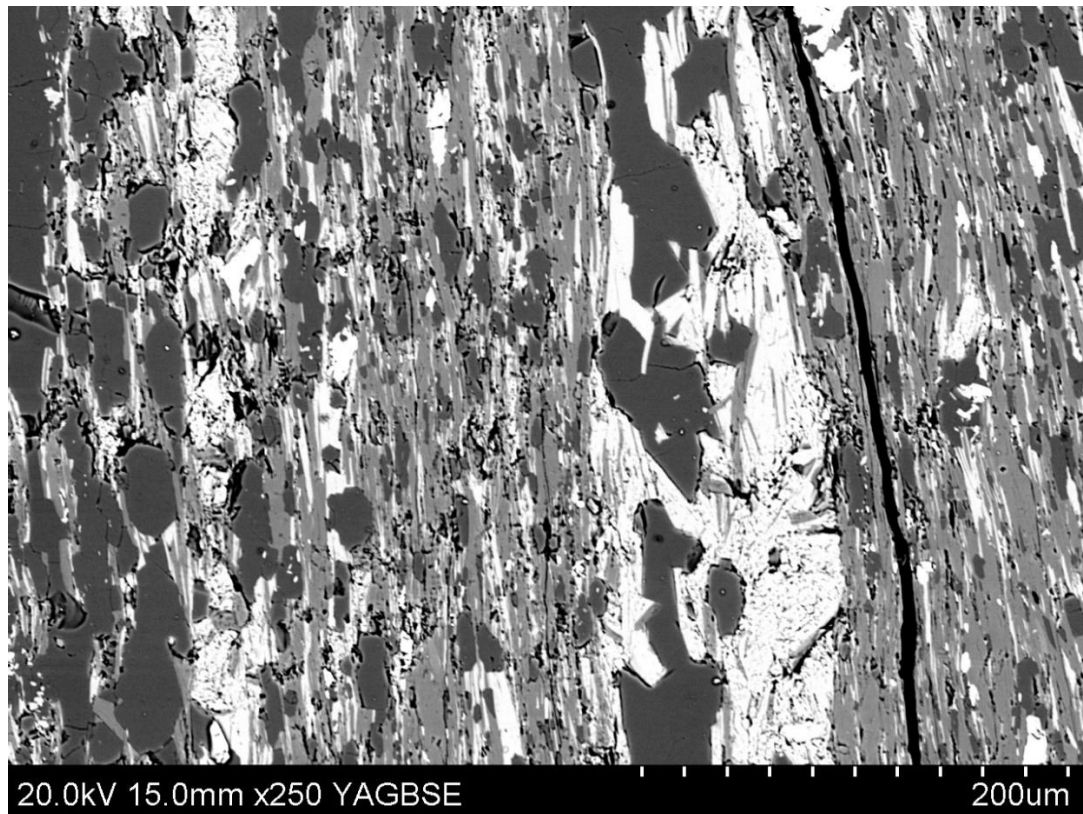


Figure 4.8: SEM image of Otago Schist (Ot.Cl.2 SEM003). Mineralogy: black=hole, dark grey = quartz, grey = muscovite, very light grey = chlorite, white = apatite/opaque. This electron image displays the varying mineralogical domains; from quartz rich (far left), to chlorite & quartz dominated, to muscovite dominated, to chlorite & quartz dominated (centre), to muscovite dominated (right).

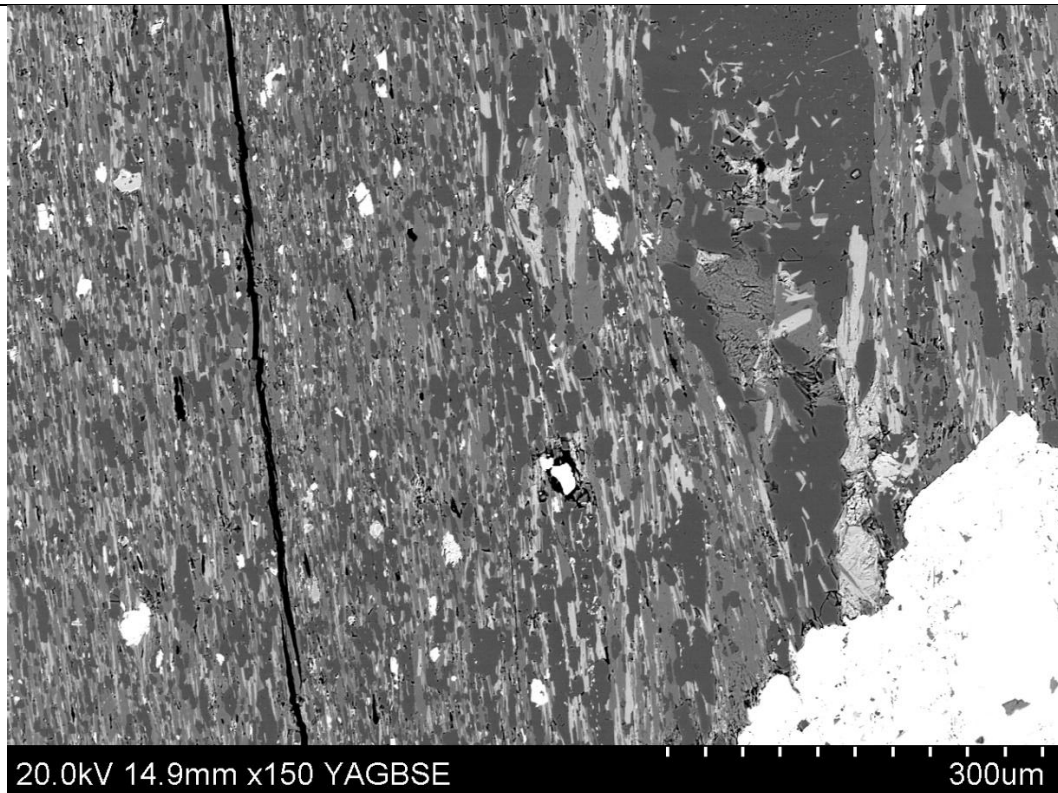


Figure 4.9: Electron Image of Otago Schist (Ot.Cl.2 SEM006), displaying a foliated matrix of quartz, chlorite and muscovite, with opaques (apatite, zircon). Coarser opaque grain (bottom right) is pyrite.

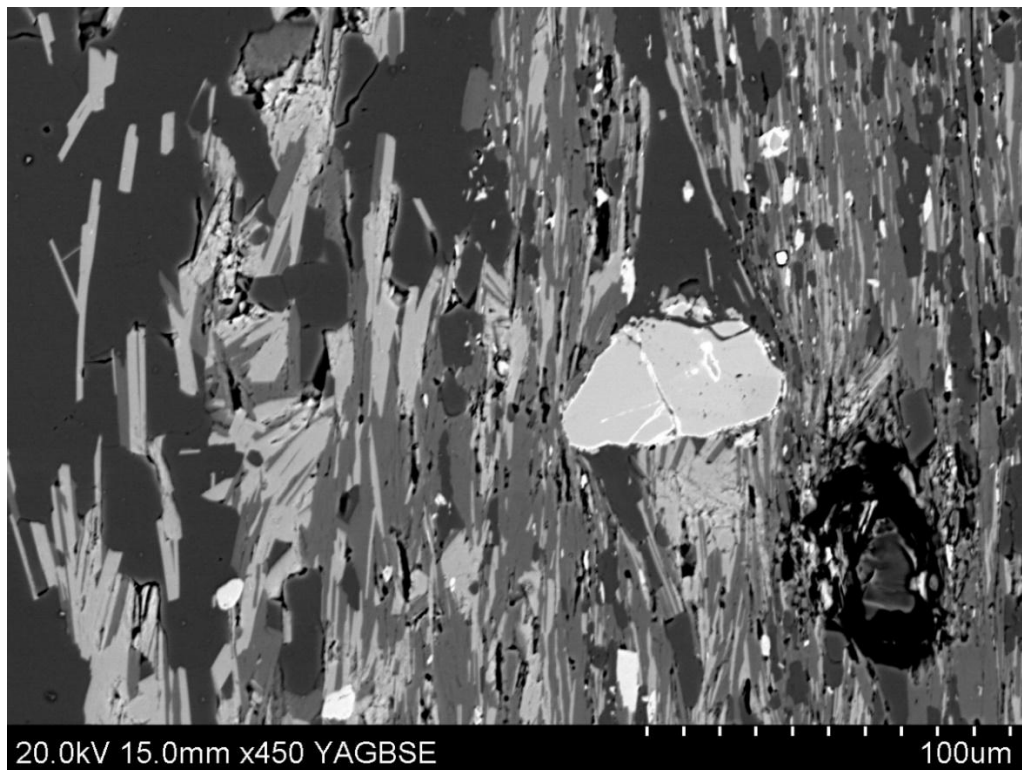


Figure 4.10: Electron Image of Otago Schist (Ot.Cl.2 SEM008). A quartz-dominated (dark-grey) section on the left contains laths of chlorite (light-grey). Chlorite and muscovite (medium-grey) then become the dominant phases, and appear foliated. A relatively coarse epidote grain is wrapped by the chlorite-muscovite matrix. The epidote grain has an allanite rim, which is present along the fracture. This is likely of hydrothermal origin. To the right there is a hole (black) within the section.

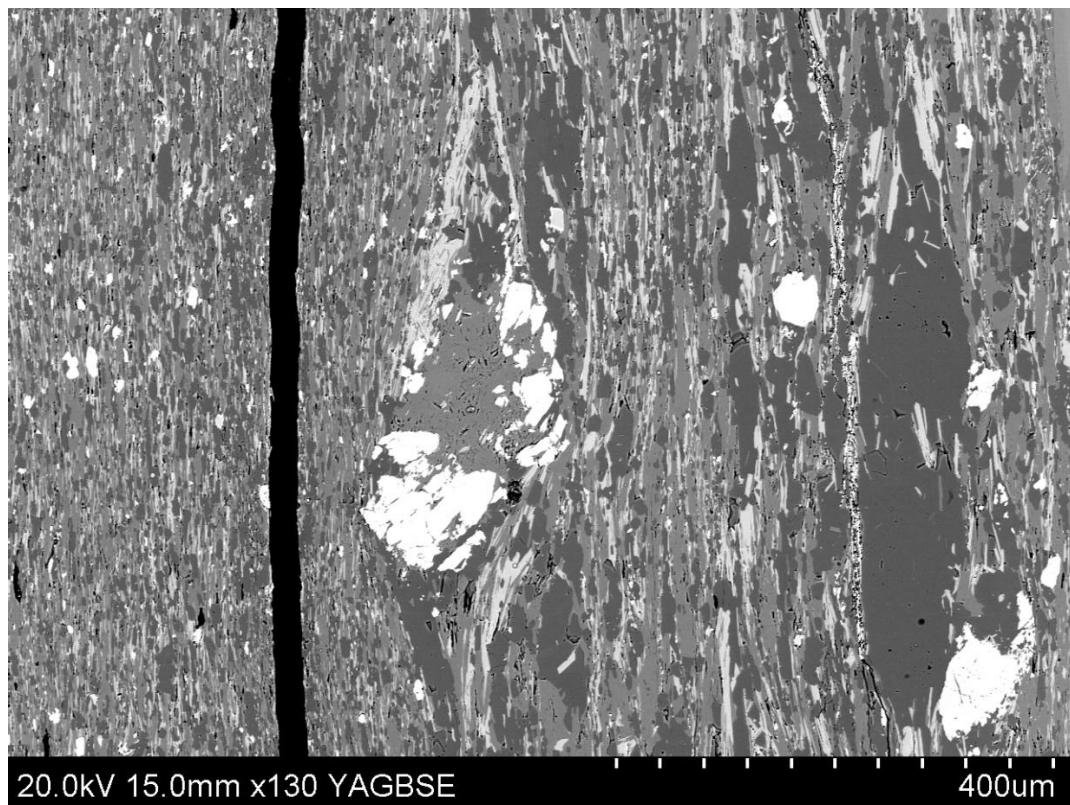


Figure 4.11: Electron Image of Otago Schist (Ot.Cl.2 SEM010), displaying varying domains of mineralogy and textures. The muscovite, and chlorite dominated matrix on the left juxtaposes the large muscovite and titanite aggregate grain (titanite appears as white). Chlorite, muscovite and quartz 'wrap' around this aggregate grain. On the right, a large, elongate aggregate of quartz grain tapers out at the bottom and top of this image.

4.2 Alpine Schist; Upper Greenschist Facies/Low Amphibolite Facies

Hare-Mare Biotite-Garnet (1.AS.H)

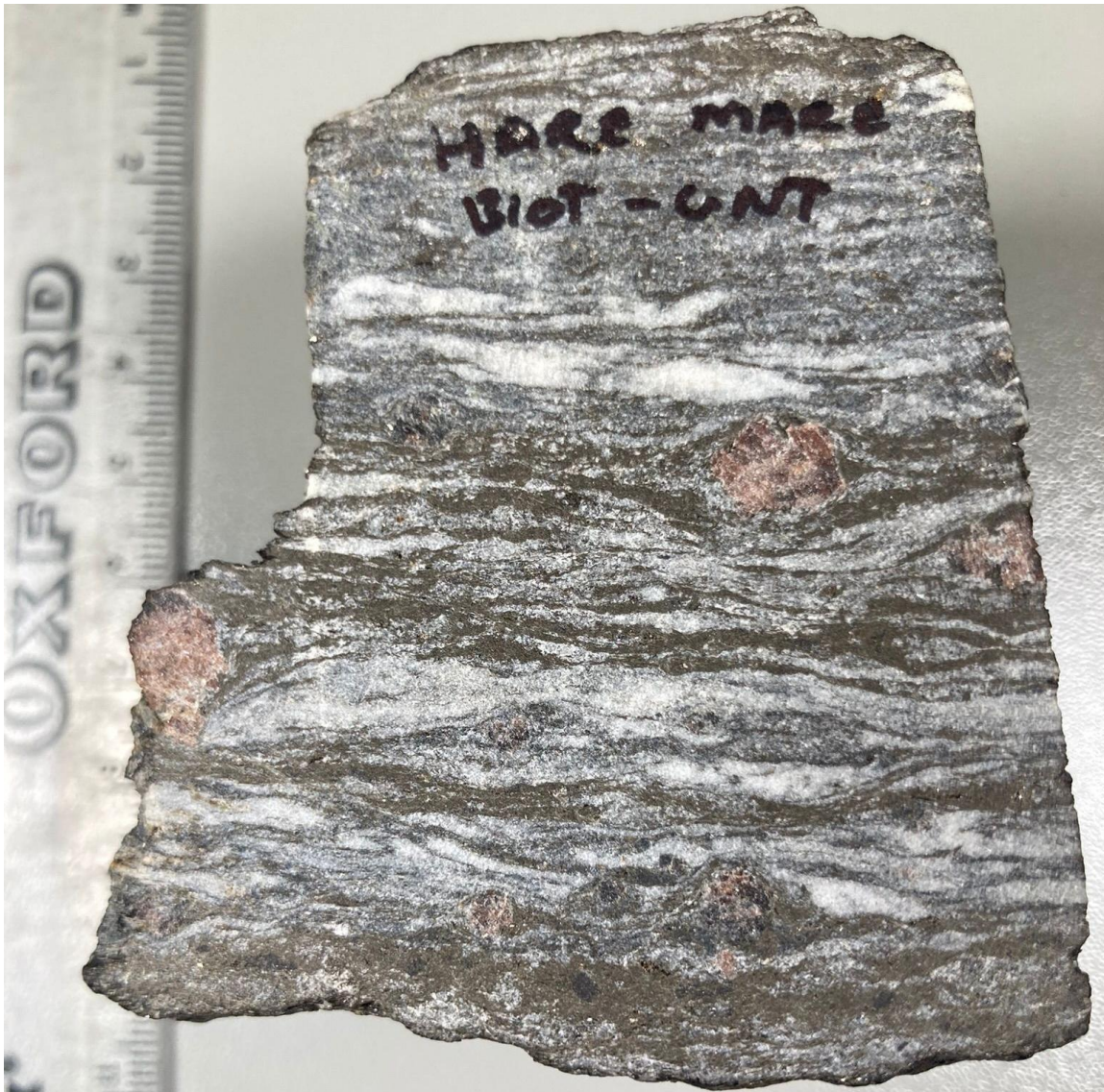


Figure 4.12: Hand specimen photo of 1.AS.H. Alternating bands of quartz + albite, and mica define a clear metamorphic foliation. Large mica porphyroblasts can be seen at hand-specimen scale (centre-bottom, to the left of partially replaced garnet porphyroblast). The observed bands wrap around garnet porphyroblasts. The garnet porphyroblast at the bottom right appears to have been extensively replaced.

Mineralogy: quartz (~40%), plagioclase (albite) (~20%), biotite (~30%), calcite (~5%), garnet (~5%), epidote, with minor muscovite, graphite, and haematite. Intense deformation has resulted in protomylonitic texture (coarse porphyroblasts, ‘smeared’ micas, intensely deformed micas, fractured feldspars, strained and recrystallised quartz). Pervasive segregation is observed, with alternating quartz and albite zones contrasting with anastomosing biotite aggregates (Figures 4.12, 4.14 & 4.17), which can contain epidote. It is important to note that no observations of muscovite in this sample were made either in thin section or using the SEM. Anastomosing biotite aggregates formed through ‘slippage’ along cleavage planes due to post-crystallisation shear (Figures 4.13, 4.16 & 4.20). The

alternating mineralogical domains are interpreted to be remnant of the earlier biotite-garnet gneiss that was present prior to protomylonitic texture. Biotite has formed at the expense of the chlorite seen in the lower greenschist facies rocks. Porphyroblasts of garnet, albite, and biotite contrast to the finer-grained quartzofeldspathic matrix. The quartz-dominated matrix is commonly elongate parallel to the fabric. This is principally attributed to post crystallisation shear (resulting in protomylonitic texture). Quartz grains are nearly all strained, evidencing post-crystallisation shear, to the extent that subgrain deformation exists. Garnet porphyroblasts are syn-kinematic, with surrounding grains ‘wrapping’ around. Pressure shadows of quartz, plagioclase and calcite are observed adjacent to porphyroblasts (Figure 4.13). Many inclusions of quartz, albite and biotite are contained within garnets, occasionally attaining ‘snowball’ textural appearance, which also supports the interpretation that these are syn-kinematic. Garnet phases occur in darker segregations and display euhedral outlines that have since been replaced by quartz, plagioclase and calcite. This results in the remaining garnet appearing subhedral/anhedral in form (Figures 4.12, 4.13, 4.15 & 4.18). The absence of muscovite in this sample is interesting, as lower greenschist facies chlorite schists contain muscovite, and Alpine Schist adjacent to the pegmatite contains muscovite. Plagioclase grains often display twinning, of which many display deformation twinning. Biotite porphyroblasts are deformed, often appearing with deformation cleavage. Micas form anastomosing ‘smears’, which are biotite dominated, caused by slippage along cleavage planes.

Calcite grains often occur in snowflake form, whereby they appear to penetrate surrounding grains (Figure 4.19). The presence of calcite is likely due to a calcareous protolith; the Alpine Schists are derived from greywackes, which included minor calcareous beds (Taylor, 1955). A prolonged and perturbed geothermal gradient may have also facilitated some ‘calcitization’ of quartz, through metasomatism (Rong & Wang, 2016). There has been significant increase in observed grain sizes from chlorite schists. This sample represents the upper greenschist/lower amphibolite facies.

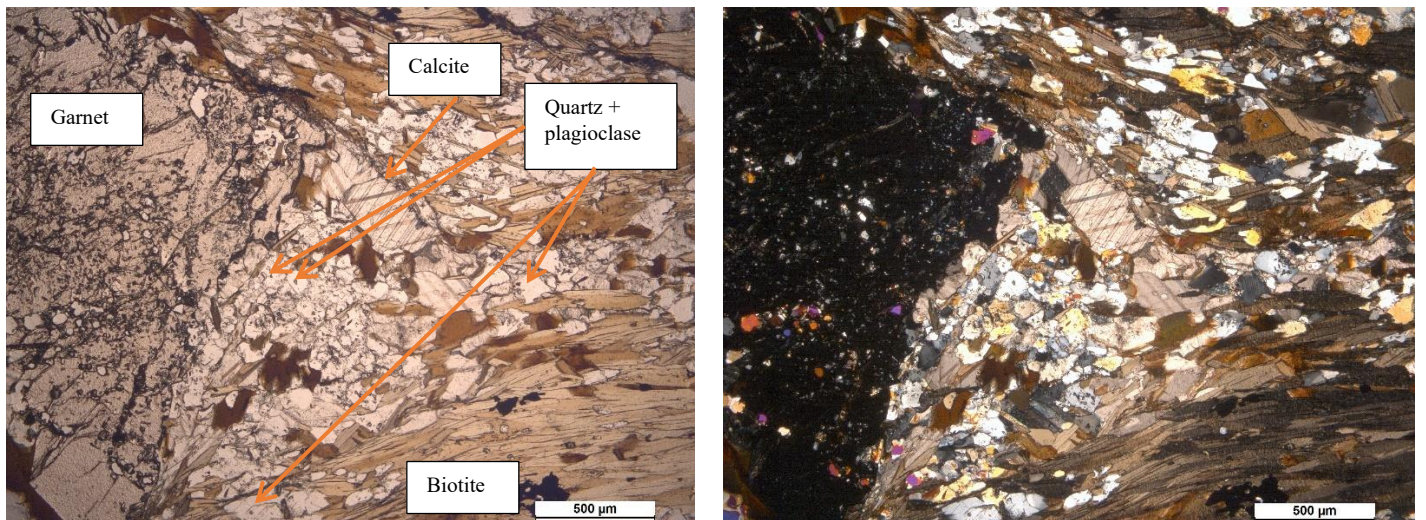


Figure 4.13: Photomicrographs of 1.AS.H, with PPL (left) and XPL (right) 80µm 'thick' section. A subhedral garnet porphyroblast (left), rich in inclusions of quartz and feldspar, contrasts with the quartz, plagioclase and calcite dominated pressure shadow (centre). This pressure shadow terminates with the enrichment of biotite in the matrix. These biotite aggregates are a significant constituent of the Alpine Schist gathered from Hare Mare. Biotite grains display significant 'slippage', with grain size and shape principally controlled by surrounding biotite grains, and shear stresses which have caused the slippage. Rhombohedral cleavages makes for easy identification of calcite grains.

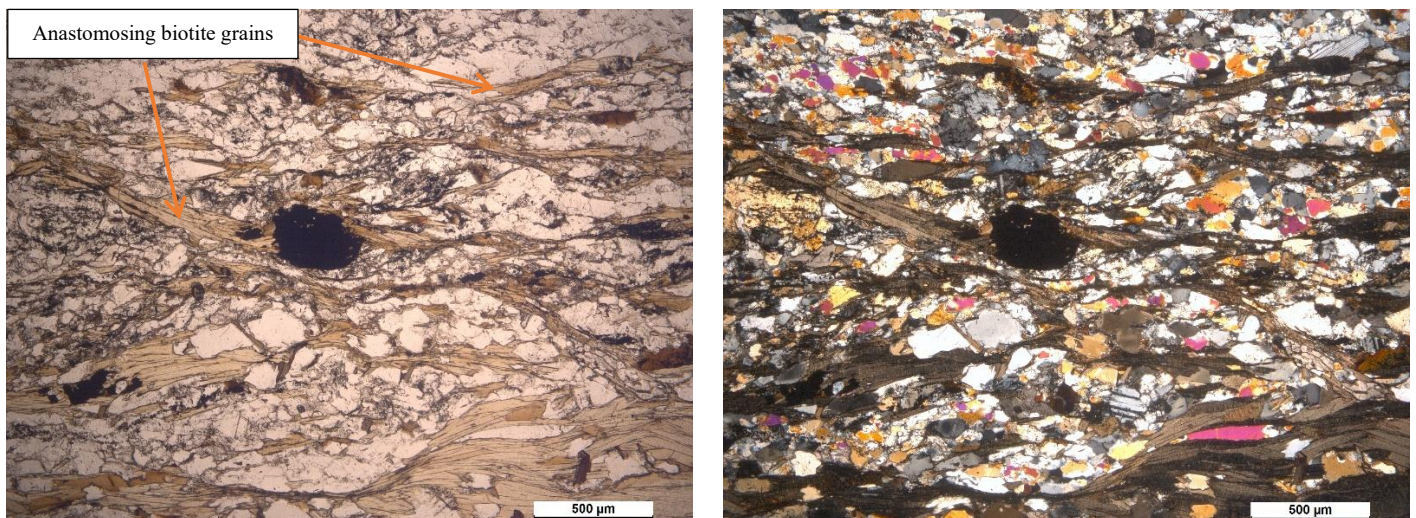


Figure 4.14: Photomicrograph 1.AS.H, with PPL (left) and XPL (right) of 80µm 'thick' section displaying the varying domains observed. The anastomosing biotite 'smears', which are ubiquitous through 1.AS.H, surround lenses of quartz and plagioclase. Within the biotite 'smear' in the middle, there is an opaque grain (Ti-Fe oxide), measuring ~450µm across.

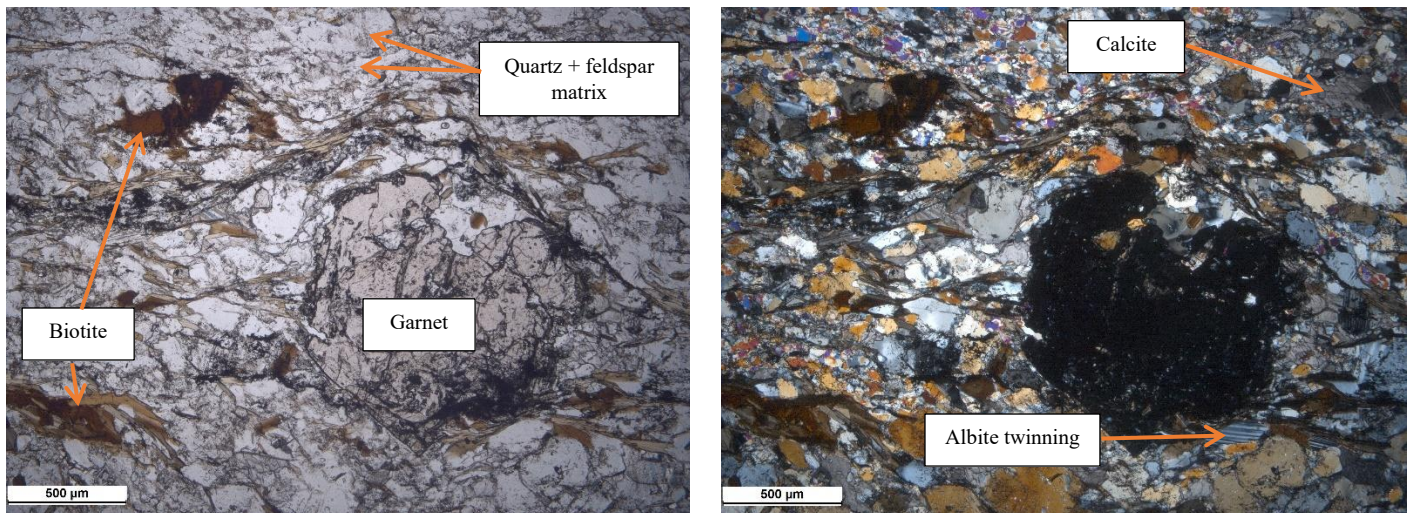


Figure 4.15: Photomicrographs in PPL (left) and XPL (right) 80µm 'thick' section, illustrating the key constituents and holistic textural variation in 1.AS.H. At the top, there is a matrix of quartz, and feldspar. Biotite separates this from the underlying quartz, feldspar and calcite matrix. The rhombohedral cleavage can be used to clearly distinguish calcite (see top right of image). The subhedral garnet porphyroblast, measuring ~1100 µm, attains pressure shadows on either side; comprised of quartz, feldspar, biotite and calcite. The paleofabric 'wraps' around the grain. To the bottom of the garnet, there is evidence for euhedral garnet growth. To the bottom right is an albite grain displaying albite twinning. Below this, is a coarser domain, with grains appearing to average ~200µm in size.

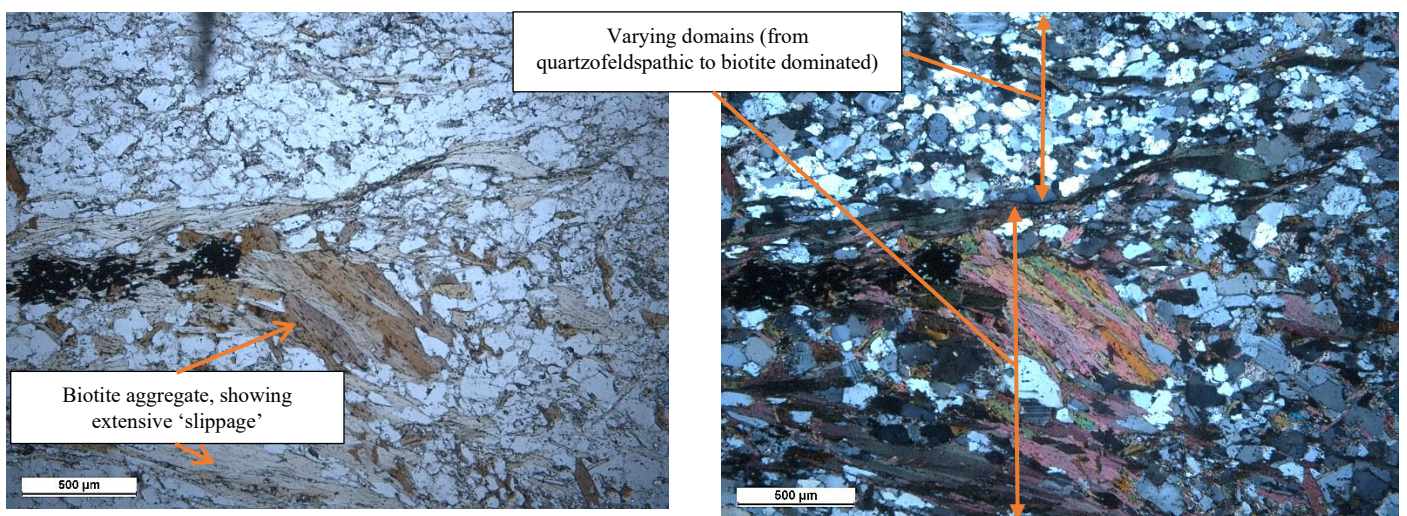


Figure 4.16: Photomicrographs (1.AS.H Thin 001) in PPL (left) and XPL (right) from 40µm 'thin' section. Showing varying domains from quartzofeldspathic to biotite dominated. Note how the biotite is deformed, with notable 'slippage' along cleavage planes. In the middle, biotite has formed an aggregate texture.

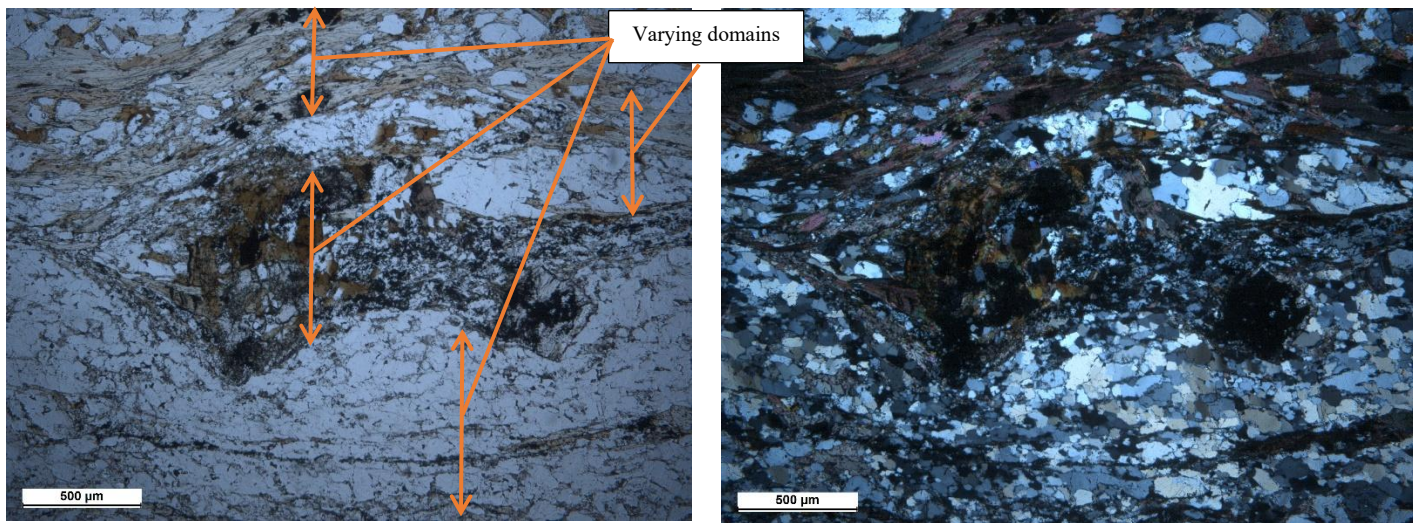


Figure 4.17: Photomicrographs (I.A.S.H Thin 002) in PPL (left) and XPL (right) from 40µm 'thin' section. Varying domains, from biotite dominated at the top, to biotite + plagioclase, to an aggregate augen of garnet, biotite, feldspar, and opaques/holes, to quartzofeldspathic matrix toward the bottom. The central section displays evidence of alteration, possibly saussurite.

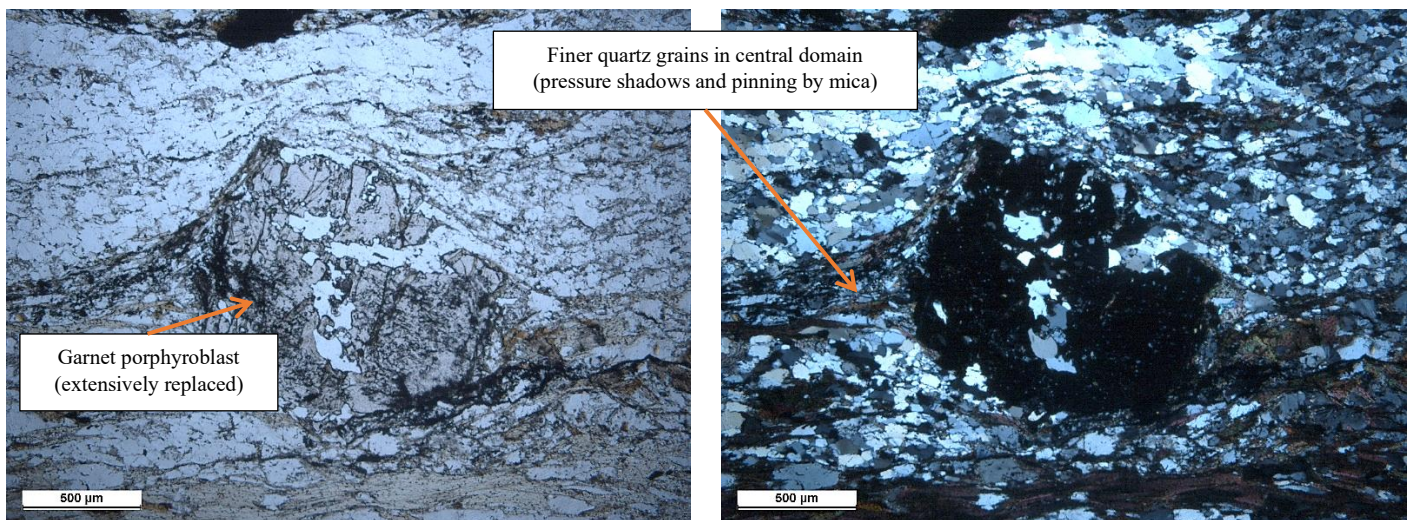


Figure 4.18: Photomicrographs (I.A.S.H Thin 004) in PPL (left) and XPL (right) from 40µm 'thin' section. Note the variation in size of quartz grains; the domain at the top has larger grains, whereas in the pressure shadows and surrounding mica grains, these quartz grains are smaller. The garnet porphyroblast has been extensively replaced.

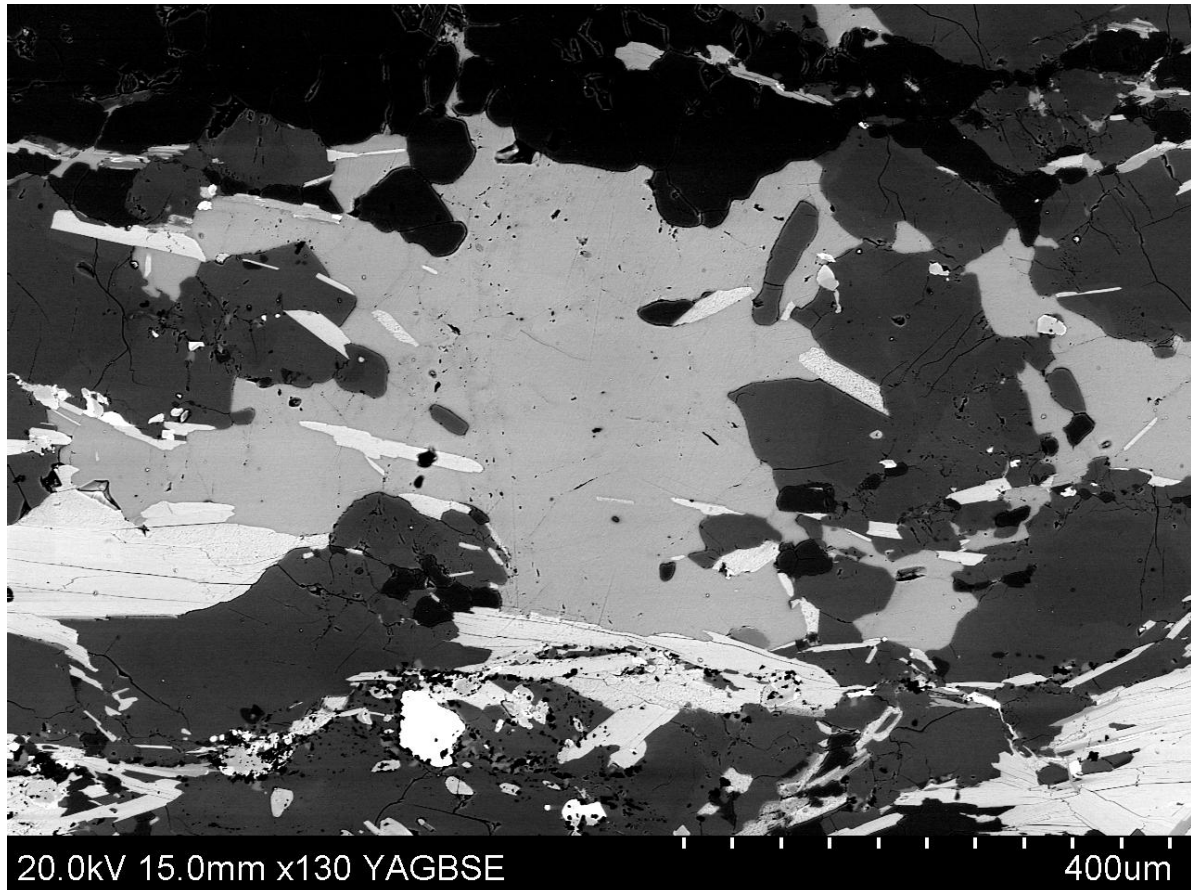


Figure 4.19: Electron Image (1.AS.H.002) displaying holes (black), quartz (very dark grey), albite (grey), calcite (lighter grey – middle of image), biotite (light grey). The calcite appears snowflake in form, with branches intruding into surrounding matrix, and contains inclusions of biotite, quartz, and albite. The snowflake form may indicate calcite replacing quartz (Rong & Wang, 2016). Biotite appears fractured, with significant ‘slippage’ along cleavage planes; indicative of shear strain. Toward the top of the calcite grain, quartz lobes ‘penetrate’ the calcite grain, indicating simultaneous growth.

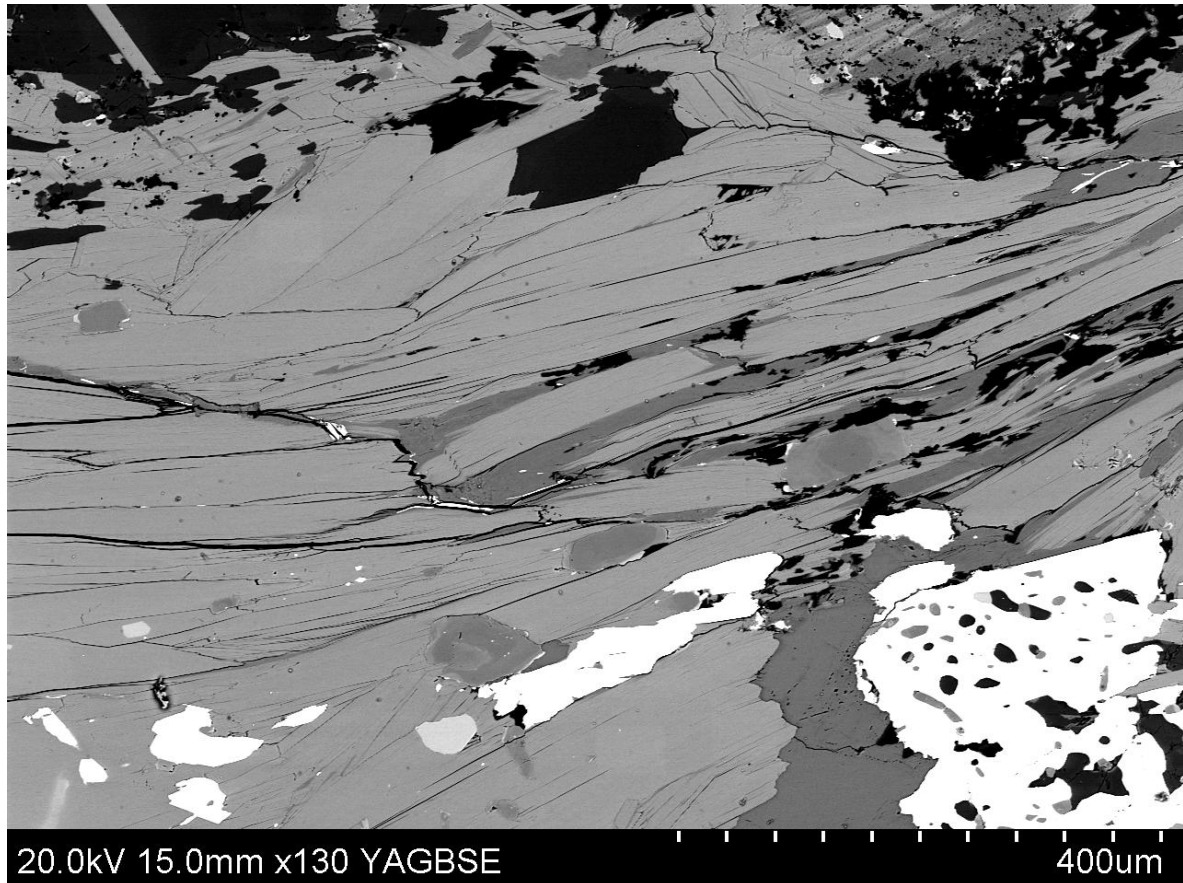


Figure 4.20: Electron Image (I.A.S.H.003) displaying the 'aggregate' nature of the biotite grains within I.A.S.H. This texture is primarily interpreted to have been derived from the strain, resulting in 'smearing'/'slippage'. Along the cleavage planes, feldspar has formed (mid-grey). To the bottom right, an ilmenite grain forms a vermicular texture, reminiscent of myrmekite, containing interlinking inclusions of quartz, albite, and biotite. The ilmenite also appears within the biotite aggregated 'smears'.

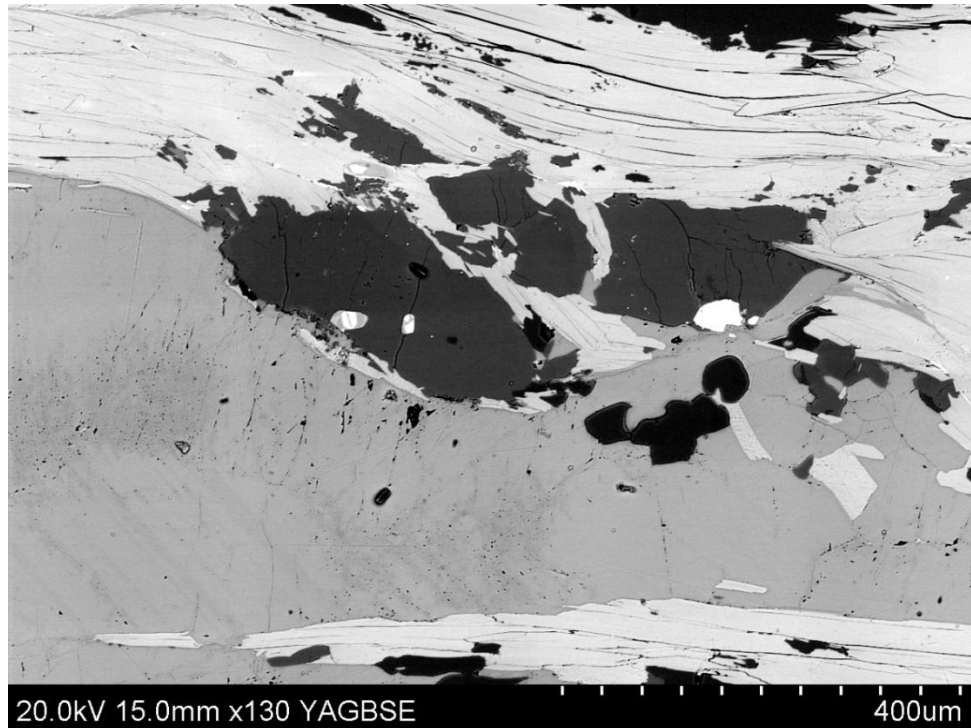


Figure 4.21: Electron Image (1.AS.H.010) showing an aggregate biotite 'smear'. The biotite grains are deformed but generally align in common orientation. Feldspar grains (mid-grey, centre) are cross-cut by smaller biotite grains. A large calcite porphyroblast dominates this image. Lesser quartz (dark-grey) occurs intermittently.

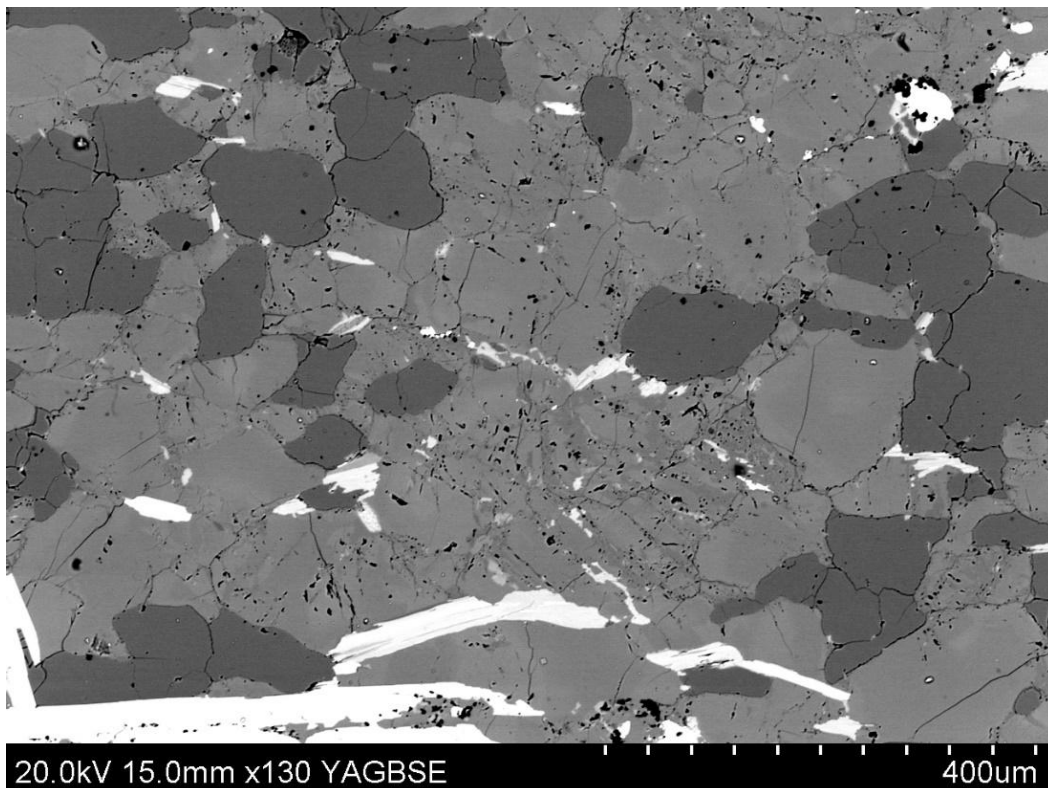


Figure 4.22: Electron Image (1.AS.H.019). Polygonal matrix grains of plagioclase and calcite form an interlocking texture throughout much of the 'matrix'. Feldspar is the dominant phase, followed by quartz in this image (dark-grey). Toward the bottom left, elongate biotite grains exist (white), which protrude into the feldspar grains.

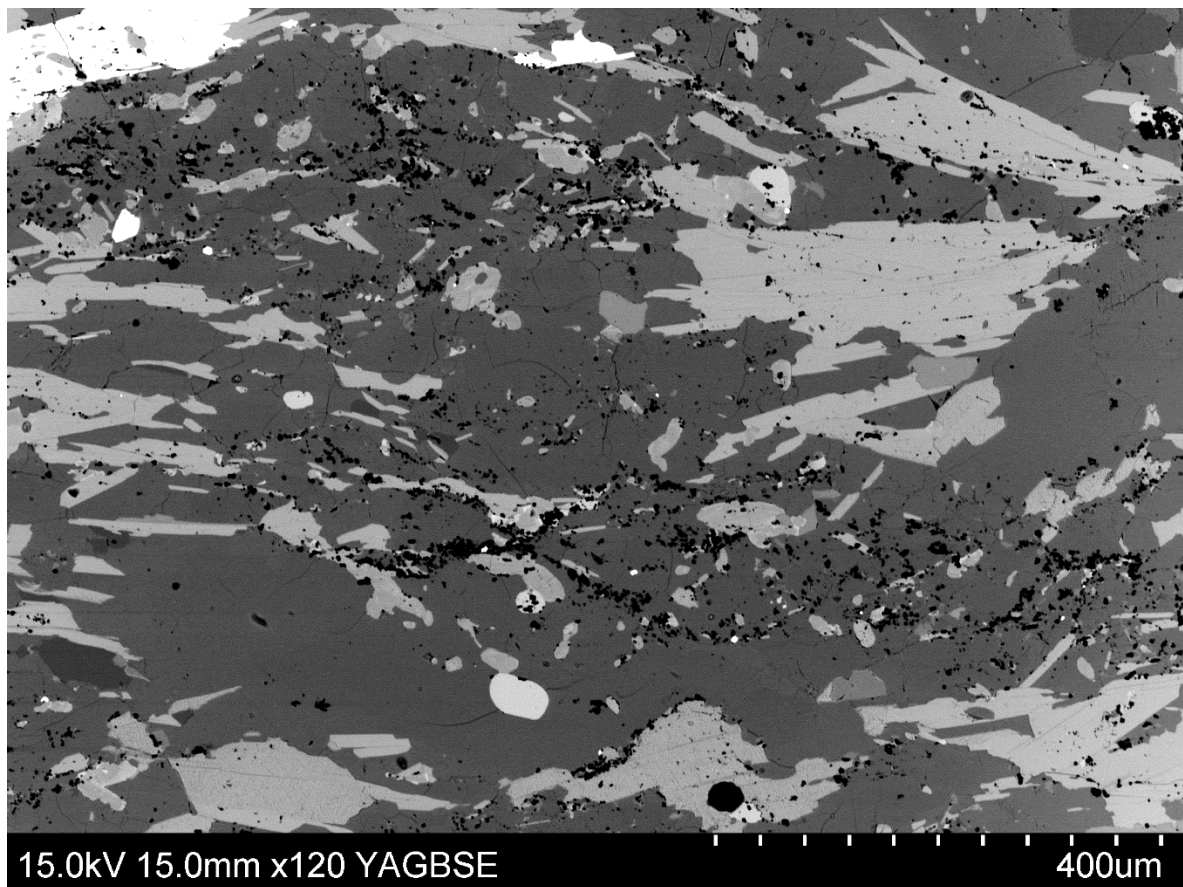


Figure 4.23: Electron Image (I.A.S.H.042) displaying how the observed matrix in I.A.S.H varies relative to previous images. The biotite grains (light grey) appear aligned right-left; and accentuate the fabric. The region is albite dominated (darker grey). Slippage can be observed along biotite cleavage planes, resulting in fragmentation of biotite grains. A fluorapatite grain exists near the bottom of the image as a 'rounded' light-grey phase. Ilmenite occurs at the top (white), with biotite existing as inclusions within the ilmenite grain.

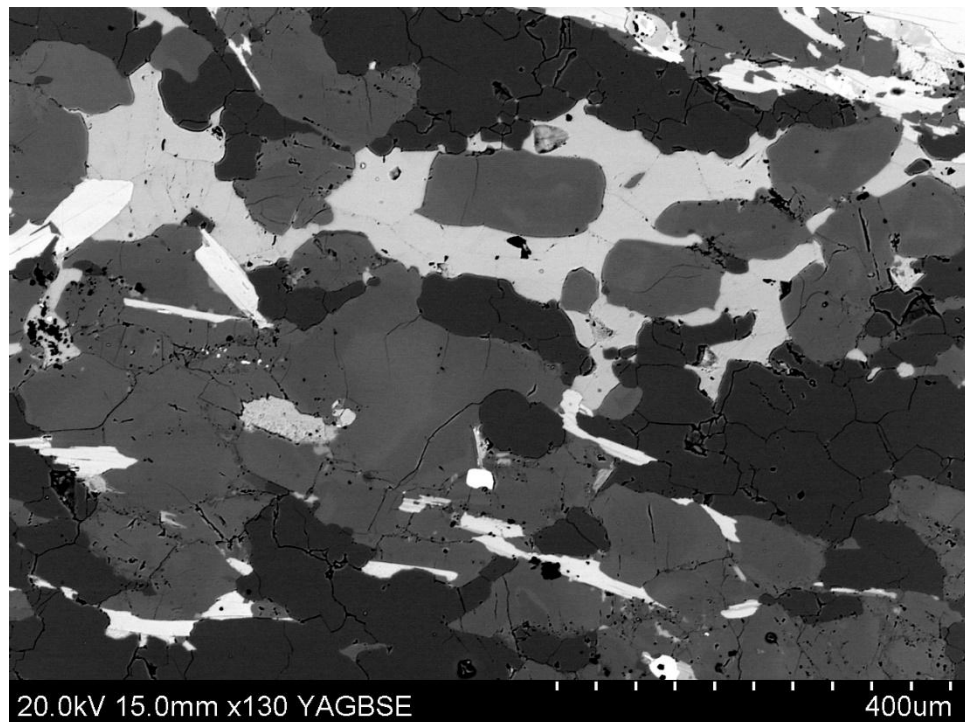


Figure 4.24: Electron Image (1.AS.H.019). Poikiloblasts of plagioclase (mid-grey) and calcite (light grey) interlock whilst quartz grains (darkest grey) occupy the rest of the matrix. Quartz grains are fractured. Laths of biotite (lightest) exist in isolation, unlike in other instances (e.g. Figure 4.21) where they are part of an aggregate.

Alpine Schist: Mataketake Pegmatite Boundary Sample (A – 1.AS & AS.MP.B)

Mineralogy (1.AS): quartz (~40%), plagioclase (~20%), muscovite (~25%), and biotite (~13%), with lesser epidote (~1%), minor apatite, Fe-oxides, chlorite, zircon, and ilmenite. Hand specimens show limited evidence of schistosity, relative to previous samples, with a distinct lack of the lighter-coloured segregations in hand specimen (Figure 4.25). The sample is dark grey, however variation in greyscale is visible, with small scale (<1mm thick) lighter streaks. Occasional garnet porphyroblasts are evident in hand specimen, but fewer than in 1.AS Hare Mare. Pink-tinted streaks of quartz highlight the fabric orientation and reach thicknesses of 5 mm. Much thinner, darker streaks also accentuate the fabric. Light coloured, translucent quartz ribbons are observed, with the widest being 2 mm (Figure 4.26). Mica porphyroblasts are visible in hand specimen (3 mm long axis) and appear deformed. Surface oxidation results in a reddish tint to weathered edges.



Figure 4.25: 1.AS (top) & 1(B)MP (bottom) Hand Specimen. Texturally distinct from the earlier schist/gneiss samples, with a general dark grey tone. Variation in colour reflects mineralogical changes, significantly, the relative enrichment/depletion of quartz ribbons. Garnet porphyroblasts are visible, and their pressure shadows are dominated by lighter coloured, translucent quartz. The pegmatite exists at the bottom (1(B)MP), and is described later (Section 4.3). This hand specimen was cut into three sections: 1.AS (comprising solely the Alpine Schist), 1.AS.MP.B (comprising both the schist and pegmatite), and 1(B)MP (comprising solely pegmatite).

Under the optical microscope, the schistose fabric is more obvious. In PPL, quartz ribbons (Figure 4.39), garnet porphyroblasts, micas and the quartzofeldspathic matrix are evident (Figure 4.26, 4.38). Mineralogical variation is clear, with contrasting domains showing differing colours and grain size/shapes.

The matrix is quartz dominated, generally occurring as a polygonal matrix aggregate (Figures 4.30 & 4.31). Many matrix quartz grains are texturally pinned by micas oriented parallel to the fabric, as the quartz attempts to achieve its lowest free energy state. Porphyroblasts of muscovite, plagioclase, and the occasional garnet or biotite contrast with the finer-grained quartzofeldspathic matrix (Figure 4.26, 4.30, 4.31, 4.36, 4.37, 4.40 & 4.42). Muscovite porphyroblasts are deformed, with slippage along cleavage planes common (Figures 4.37 & 4.42). Muscovite ‘smears’ evidence shear strain (Figures 4.31 & 4.32). Garnet porphyroblasts appear anhedral, with replacement to plagioclase and quartz facilitating the observed form (Figure 4.26). There is strong evidence for garnet growth being syn-

kinematic, with clear ‘snowball’ trails of inclusions, and surrounding grains ‘wrapping’ around the porphyroblasts (Figure 4.35).

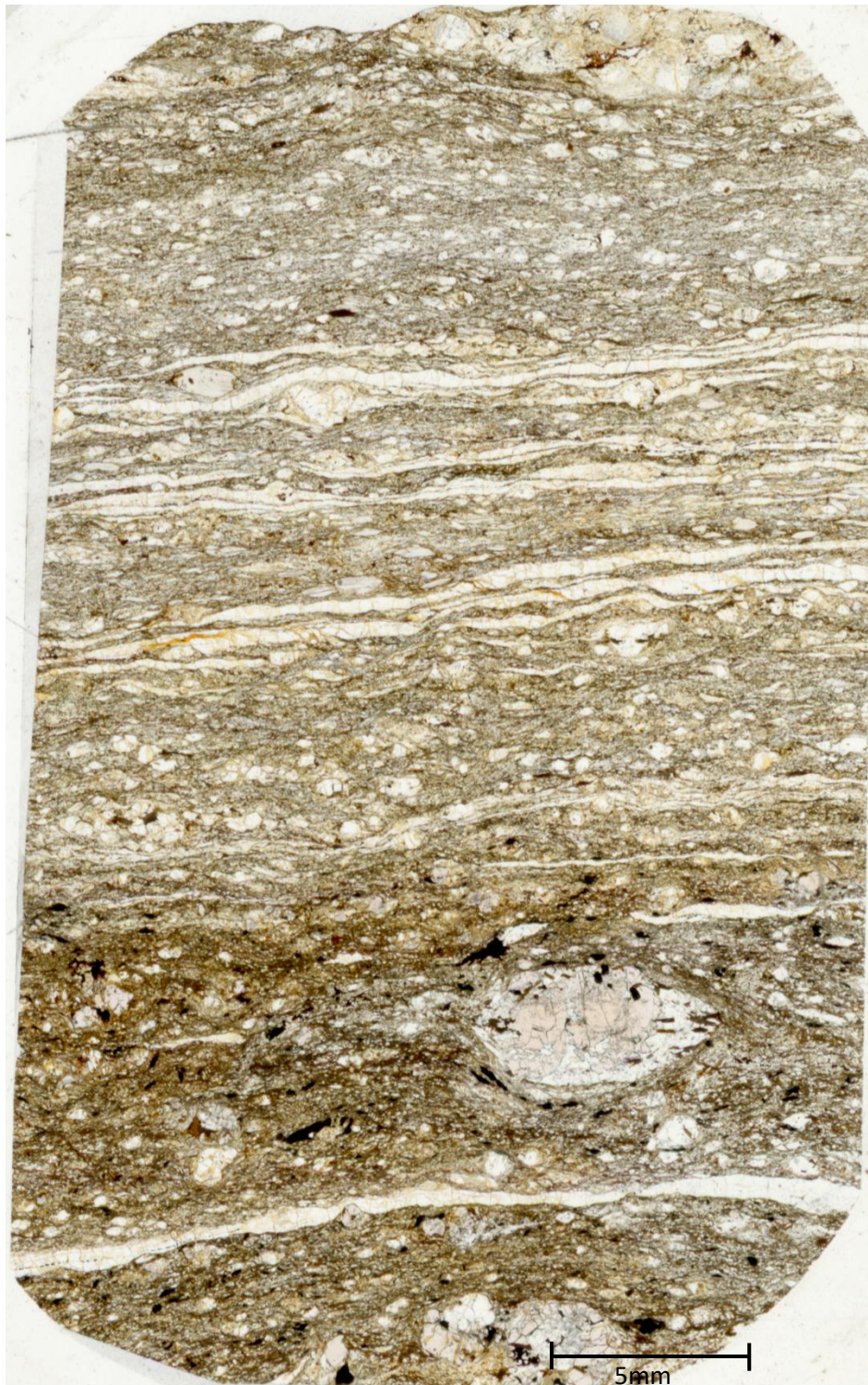


Figure 4.26: 1.AS 80um Thick Section Scan. Quartz ribbons, muscovite, and plagioclase contrast with biotite and opaques. Anhedral garnet porphyroblast is seen in the lower centre, containing inclusions of biotite, apatite and plagioclase.



Figure 4.27: 1.AS.MP.B 80um Thick Section Scan. Significant contrast from the relatively biotite-enriched Alpine Schist to the quartz-feldspar dominated Mataketake Pegmatite. Note the absence of biotite streaks in the pegmatite. Microscopy identifies muscovite-dominated streaks in the pegmatite. The most notable change apart from colour, is grain size. Large porphyroblasts of feldspar and muscovite are deformed. The former show bookshelf fracturing, and kink-banding. The latter appear as mica 'fish'; with undulating fractures along deformed cleavage planes.

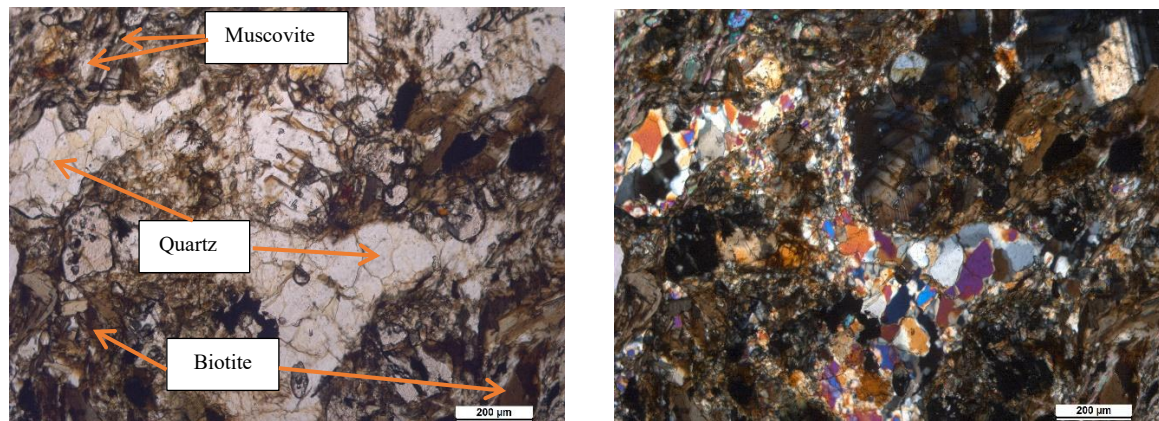


Figure 4.28: PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section). PPL shows the proliferation of biotite, which is not as abundant in the pegmatite. Quartz displays subgrain deformation.

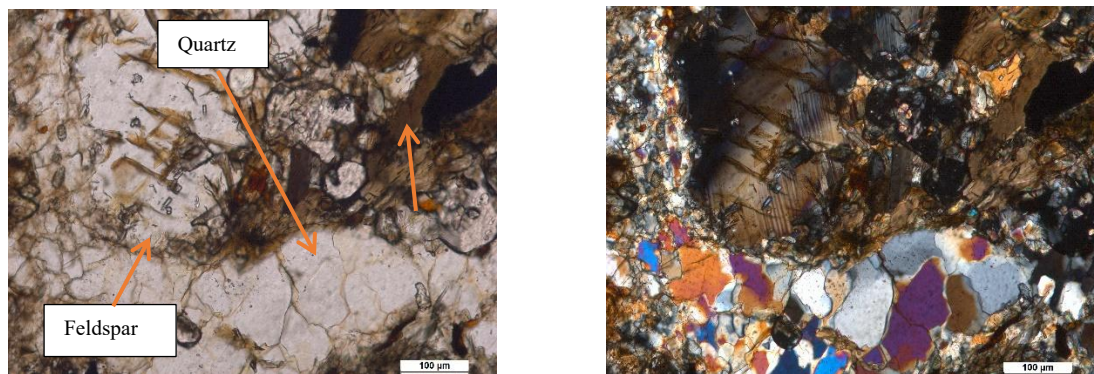


Figure 4.29: PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section). A close-up of same view as figure 4.28 showing the deformation twins (note how they pinch out) in the feldspar (centre).

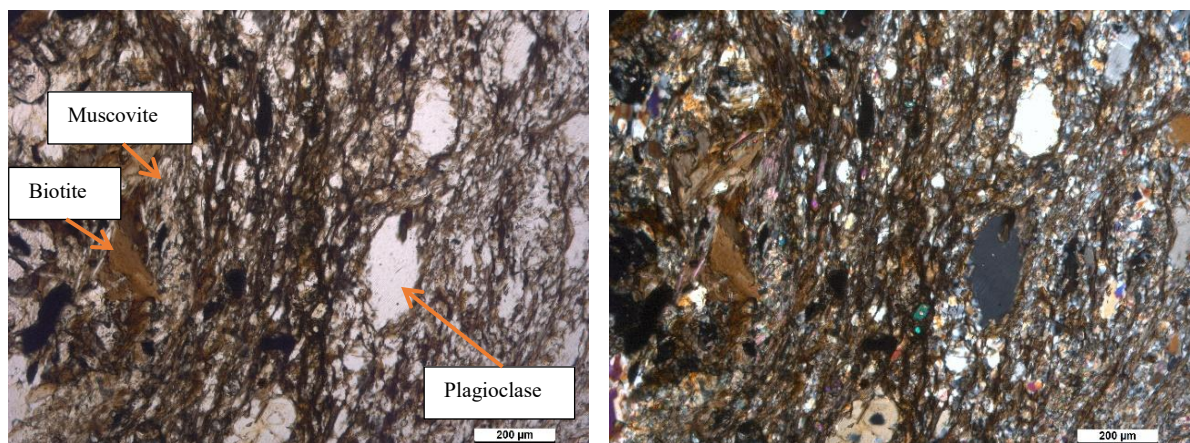


Figure 4.30: PPL (left) and XPL (right) of 1.AS.MP.B.2 (80µm Section). PPL shows biotite grains (brown) on the left of the image. These vary in intensity of their pleochroic colour due to variable crystallographic orientation. Thin folia of muscovite exist either side of these grains and appear as green and pink interference colours in XPL. Mica within this image often appears as thin folia, which highlight fabric orientation. The matrix is quartzofeldspathic, with the mica grains pinning quartz grains and inhibiting growth. To the mid-right a plagioclase grain appears grey in XPL. To the bottom of this grain, albite twinning can be seen, although these twins are deformed (Figure 4.30.2 (below)) Other plagioclase 'porphyroblasts' occur in the right section of this image, and the biotite folia can be seen wrapping around these grains.

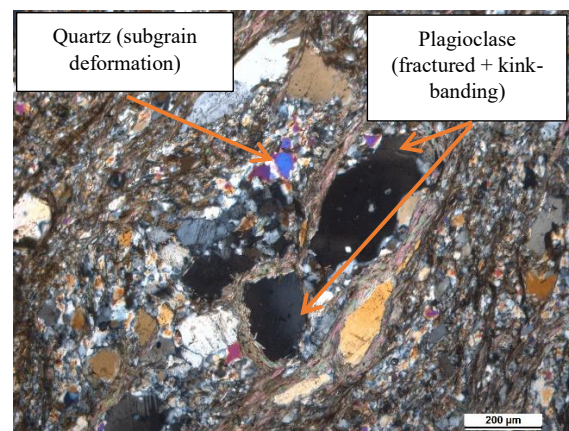
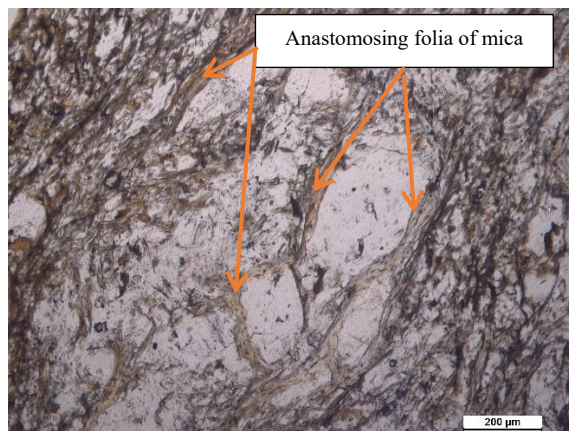
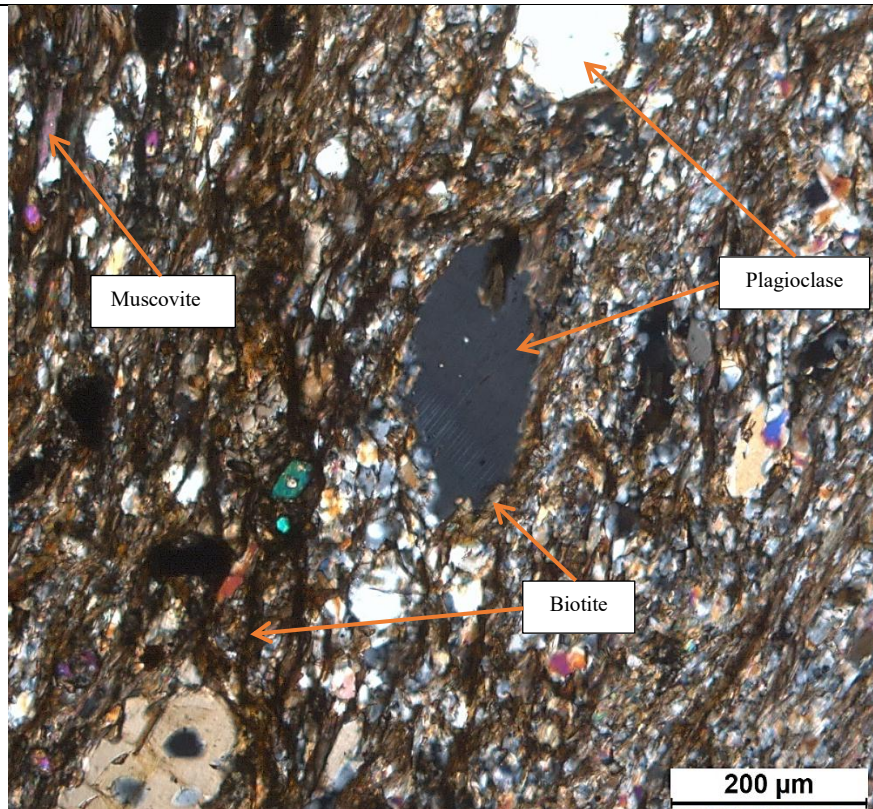


Figure 4.31: PPL (left) and XPL (right) of 1.AS.MP.B.3 (80μm Section). Feldspar porphyroblasts define this image. They are fractured, and display kink-banding; indicating deformation. Deformation twins can occasionally be identified. In the centre of the image, quartz grains appear blue-purple in XPL. These grains show sub-grain deformation. Note how these grains are coarser than quartz in the matrix – this is due to less mica being present, facilitating the growth of quartz. In PPL one can clearly see the micaceous folia wrapping around feldspar porphyroblasts in the centre of the image. These folia likely formed due to slippage along mica cleavage planes during a shearing event.

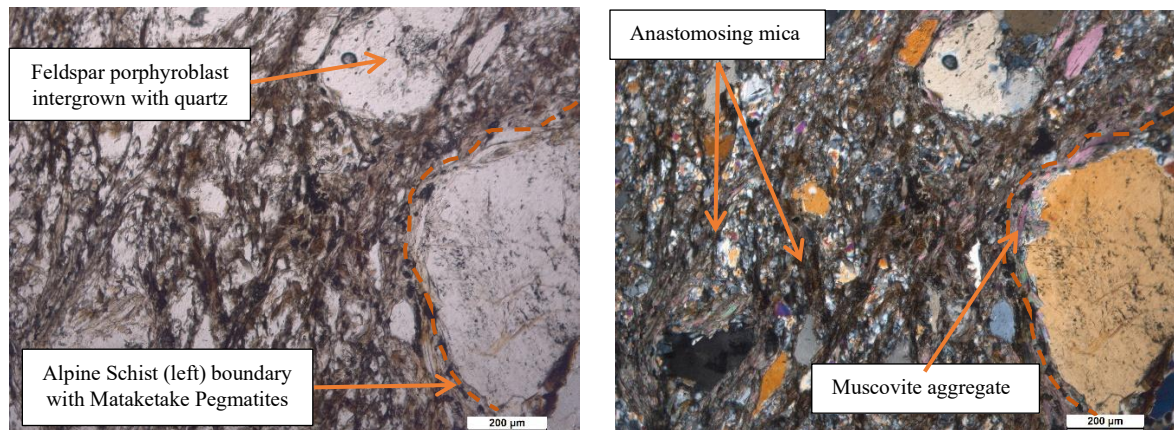


Figure 4.32: PPL (left) and XPL (right) of 1.AS.MP.B.4 (80µm Section). This image contains the boundary (orange dashed line) with the Mataketake Pegmatite (right). The schist has a quartzofeldspathic matrix, with anastomosing micaceous aggregate folia (biotite-dominated in this instance) wrapping around feldspar porphyroblasts. The feldspar porphyroblast to the top right shows intergrowth with quartz, evidenced through the dark-grey interference colours. On the schist-pegmatite border, a muscovite aggregate wraps around the pegmatitic feldspar porphyroblast, but also juts into the grain.

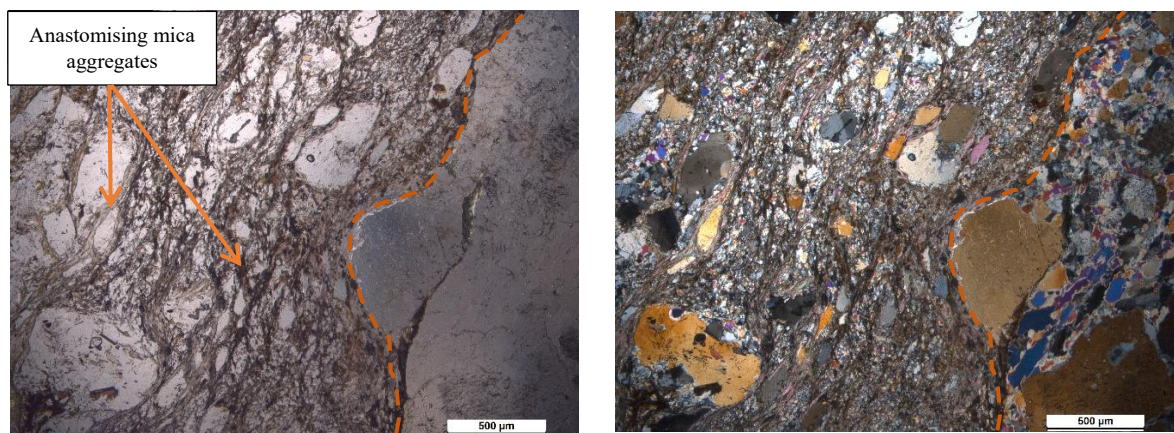


Figure 4.33: PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section). PPL evidences the differing textures and mineralogy. The pegmatite (right) is dominated by quartz and feldspar, with much less biotite than the schist (left).

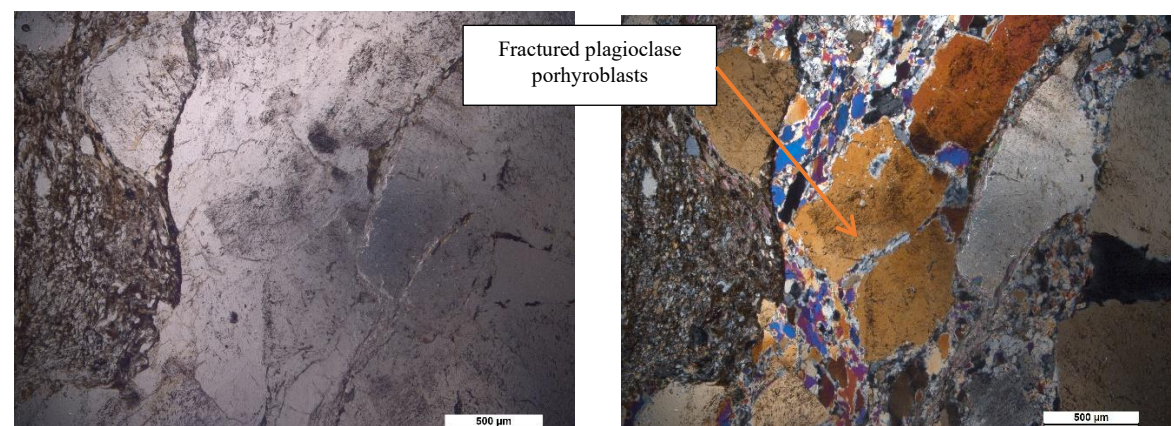


Figure 4.34: PPL (left) and XPL (right) of 1.AS.MP.B.1 (80µm Section). This image highlights the variance in grain size between the schist (left) and the pegmatite (right); coarse porphyroblasts of plagioclase, and much coarser quartz grains in the pegmatite contrast with the much finer schist.

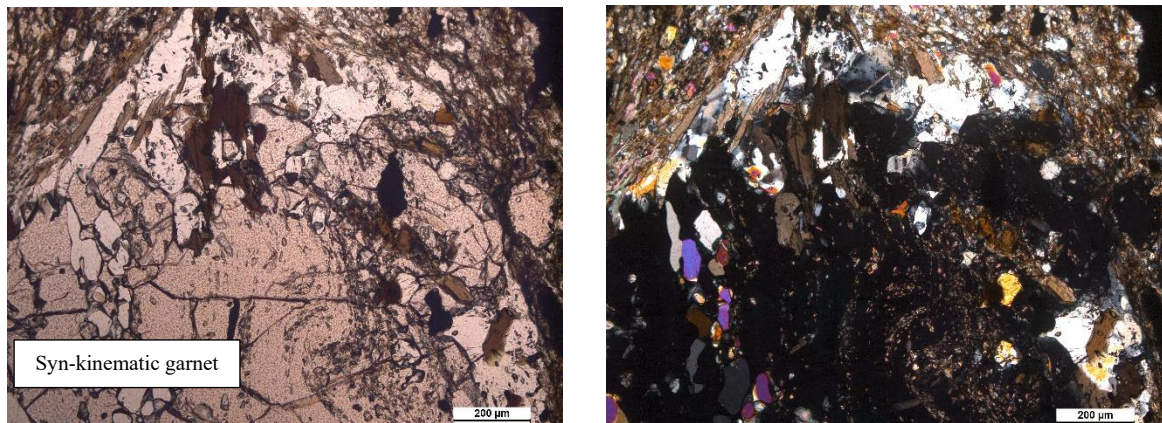


Figure 4.35: PPL (left) and XPL (right) of 1.AS.1 (80µm Section). Syn-kinematic garnet with spiral inclusion trail of graphite inclusions (lower centre), with large inclusions of biotite, feldspar, and quartz.

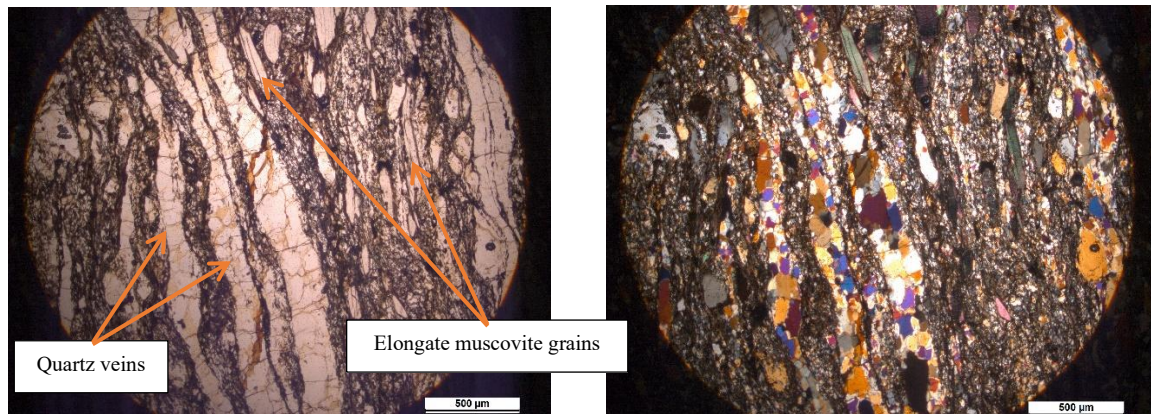


Figure 4.36: PPL (left) and XPL (right) of 1.AS.3 (80µm Section). Quartz veins define this image, with subgrain deformation seen in XPL. Note how elongate muscovite grains also align with these quartz veins (e.g. top centre), accentuating the fabric of this specimen. Feldspar grains are wrapped by the matrix. Muscovite grains are deformed, with kinked-extinction and bent cleavage planes.



Figure 4.37: PPL (left) and XPL (right) of 1.AS.4 (80µm Section). A closer look at a quartz vein (bottom left) and muscovite porphyroblasts. In the centre, a muscovite porphyroblast is twinned along its basal plane (001).

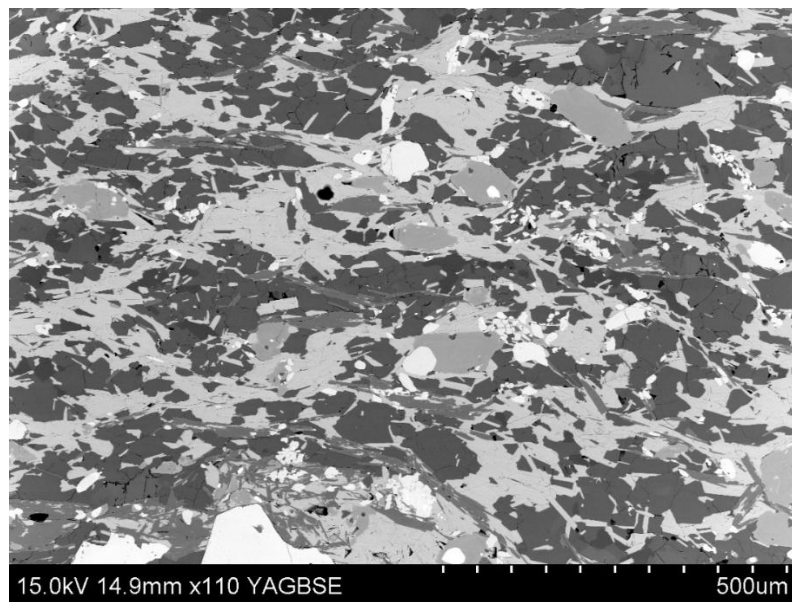


Figure 4.38: Back-scattered electron Image of Alpine Schist (I.AS.001). This image displays the matrix within the Alpine Schist. Black = holes, Dark grey = quartz, medium-dark grey = plagioclase, grey = muscovite, medium-light grey = epidote, light grey = biotite, white = ilmenite/titanite/(fluor)apatite/garnet. This matrix contains anastomosing biotite, which wrap around feldspar grains. Muscovite occurs to a lesser extent than biotite, although the grayscale makes muscovite less pronounced.

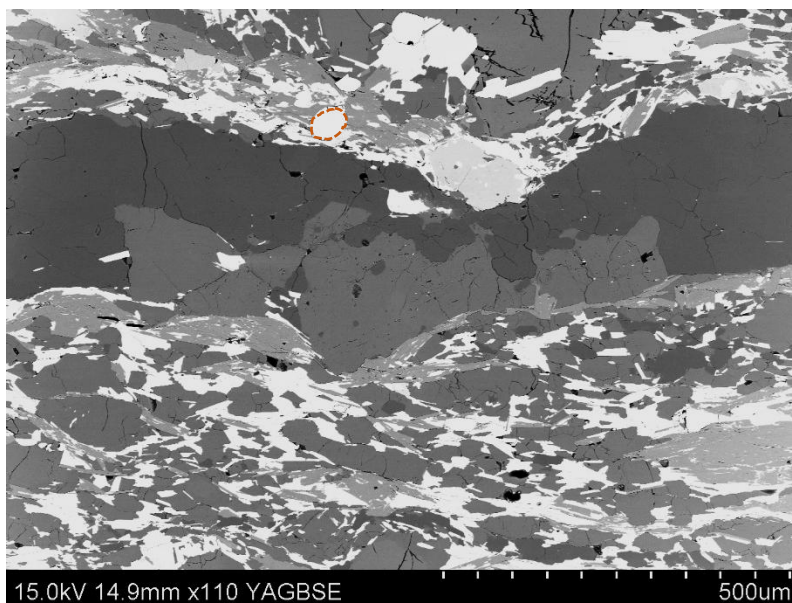


Figure 4.39: Back-scattered electron Image of Alpine Schist (I.AS.003). Black = holes, dark grey = quartz, medium-dark grey = plagioclase, medium-light grey = muscovite, light grey = epidote, grey-white = biotite, white = opaques (Fe-oxides & (fluor)apatite). Contrasting domains within the schist; a quartz-vein, which contains plagioclase grains, bisects this image. An epidote grain occurs within the depression atop this vein, with an Fe-oxide (white) just beneath it. The epidote grain lies amongst a biotite and muscovite dominated section. A 'rounded' fluorapatite grain lies above the quartz ribbon, contradicting the foliated, elongate mica grains (dashed lines). Above the epidote, lies a fractured plagioclase porphyroblast, with biotite grains intruding. Beneath the vein, deformed muscovite grains contain biotite on fractured cleavage planes. Aside from micas, plagioclase is the dominant matrix grain here, with the occasional quartz grain.

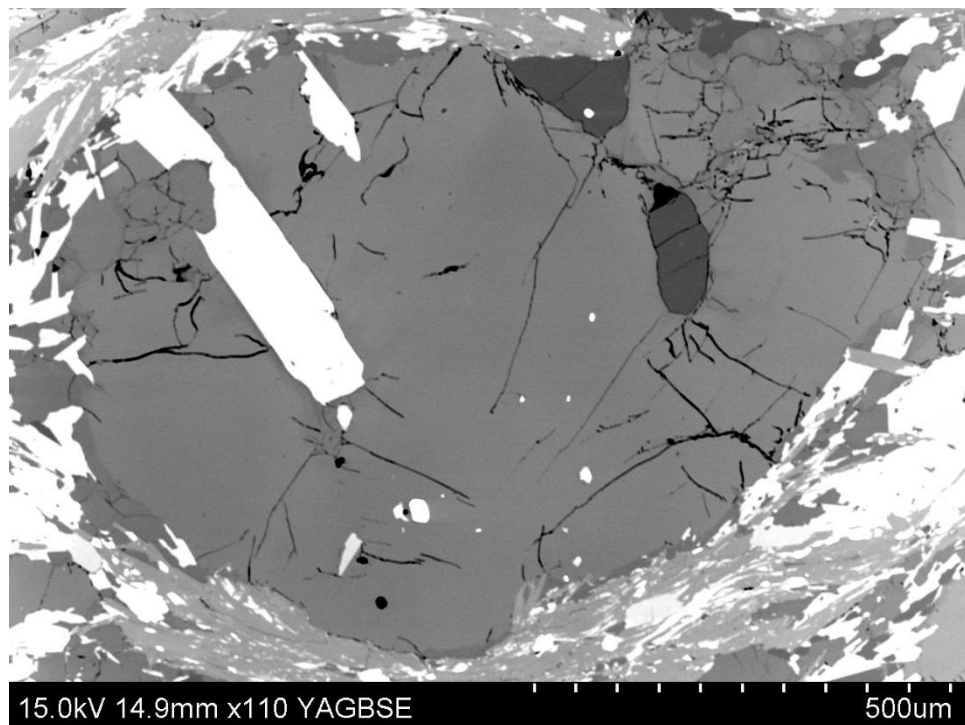


Figure 4.40: Back-scattered electron Image of Alpine Schist (1.AS.005). A fractured plagioclase porphyroblast occurs with a thin rim (slightly darker grey) of more albitic plagioclase. A large lath of biotite is included by this plagioclase grain, with other inclusions of quartz (to the right, dark-grey), and epidote (beneath the biotite, very light grey). The plagioclase grain is bordered by a micaceous aggregate, a common feature in the Alpine Schist.

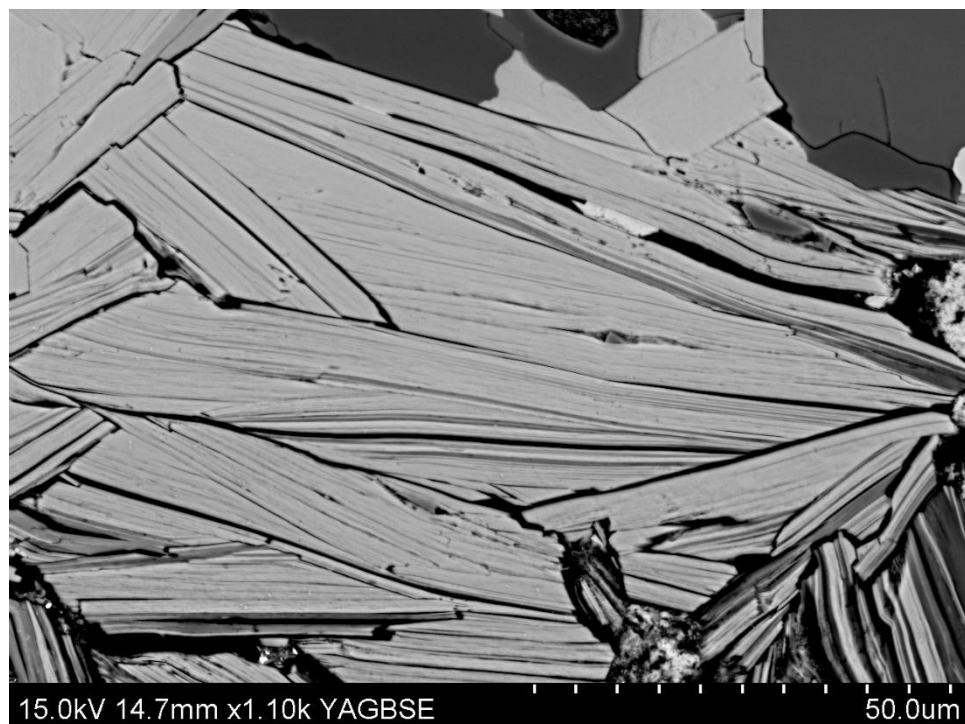


Figure 4.41: Back-scattered electron Image of Alpine Schist (1.AS.018). A closer look at an aggregation of biotite grains showing common orientation.

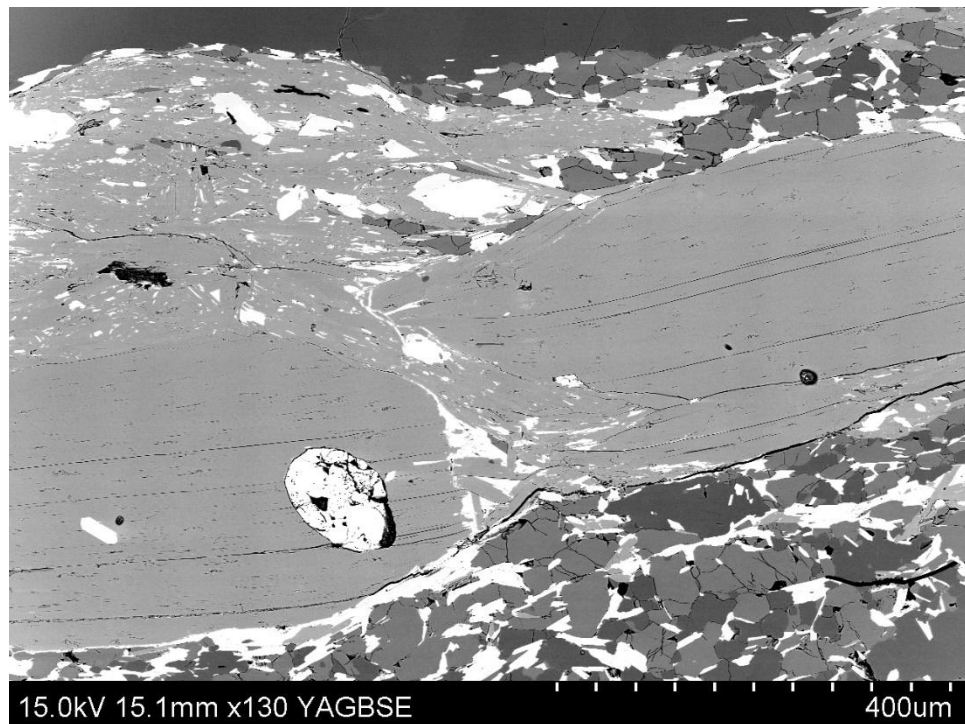


Figure 4.42: Back-scattered electron Image of Alpine Schist (I.AS.031). Two relatively coarse muscovite grains appear interlinked yet crosscut by an aggregate of finer muscovite and biotite grains. Above the muscovite on the left, this aggregate mica texture is dominant. The micaceous grains are commonly fabric-oriented; however, they occasionally occur as a decussate texture. We interpret these textures as evidence of post-formation shearing, which has resulted in slippage along micaceous cleavages, forming these aggregates of smaller grains. Deformation is also evident within the two dominant muscovite grains in the form of deformed cleavages and inclusions. A biotite inclusion can be seen on the left, with a notable apatite inclusion to the right. At the very top of the image is a quartz vein. Beneath this lies the micaceous aggregate, along with a quartz-feldspar-mica matrix to the top-right of the image. At the bottom of the image, this micaceous-quartzofeldspathic matrix continues. Note the prevalence of biotite grains, which likely inhibited quartz growth due to textural pinning.

1.AS.MP.B (Area 2)

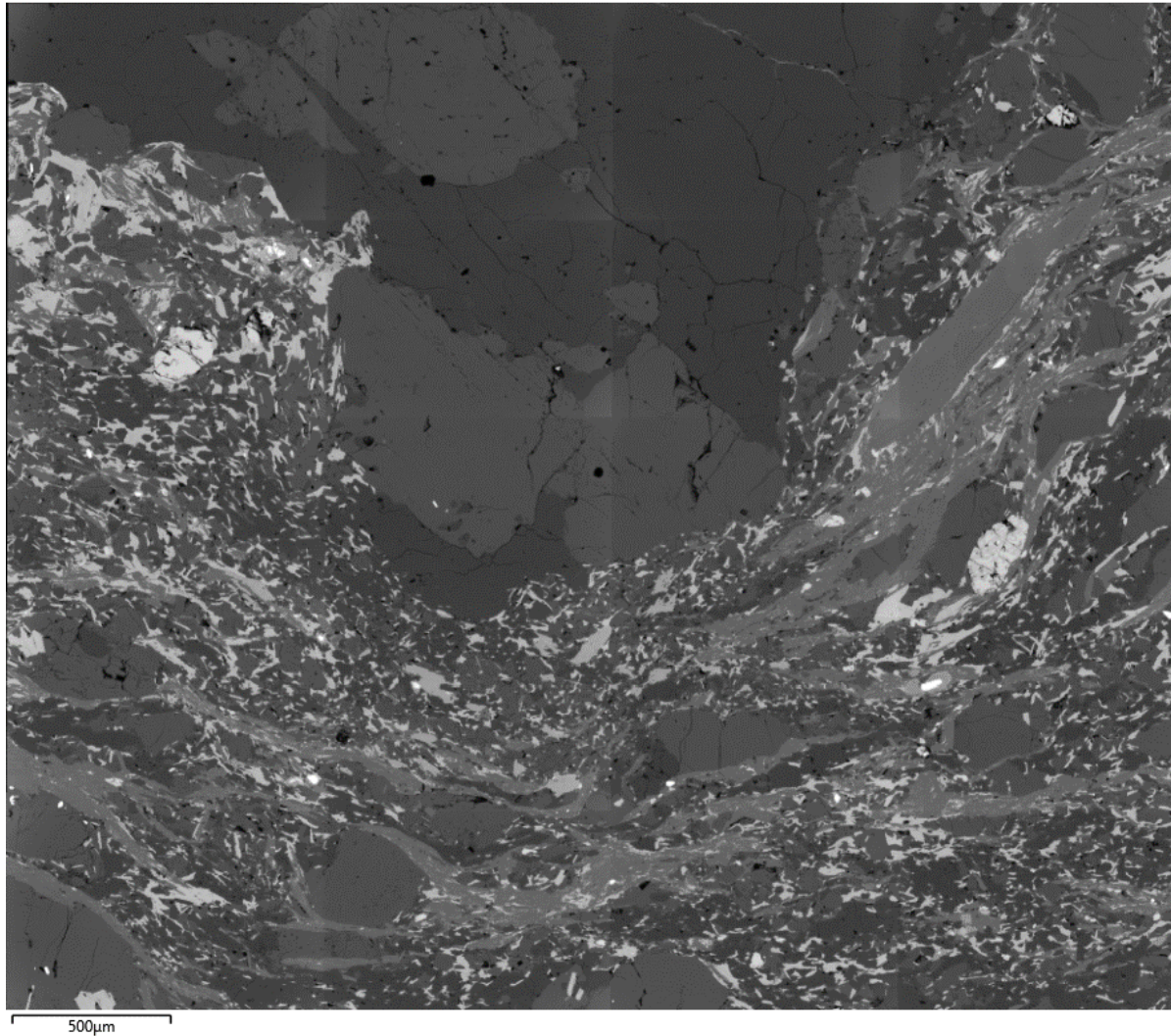


Figure 4.43: Montaged electron images of Alpine Schist and Mataketake Pegmatite boundary (1.AS.MP.B Area 2). Note the different textures, and notably the difference in grain size and mineralogy, between the schist (lower) and pegmatite (upper). The pegmatite is dominated by quartz and feldspar, and it appears to cut into the schist in this location, communicating the intrusive origins of the pegmatite. Conversely, the schist is much finer, with porphyroblasts of feldspar and muscovite. Mica aggregates anastomose across the sample, and wrap around feldspar grains. Quartz appears in the matrix, along with biotite in this section. Relatively large round grains of apatite exist within the schist. Allanite appears as the whitest colour in this image, and is surrounded by 'regular' epidote.

4.3 Mataketake Pegmatite (1(B) MP & 2MP.1)

Mineralogy: quartz (~40%), plagioclase (~35%), muscovite (~20%), biotite (~5%), with lesser chlorite, epidote, and rare apatite and zircon.

Hand specimen shows a largely white coloured rock, with contrasting black mica grains; see Figure 4.25 and Figure 4.44 (below). Mica porphyroblasts measure up to 8mm long and 3mm wide. Dark, micaceous streaks are continuous through the sample. Some phases attain a reddish-pink tint, possibly due to surface oxidation.

Observed microtextures within the pegmatite matrix are principally controlled by post-emplacement shear, producing a protomylonitic texture, and through the varying textural qualities of structurally anisotropic (muscovite, biotite) and structurally isotropic (quartz) phases. The matrix is quartz-dominated (Figures 4.46, 4.48, 4.50, 4.51, 4.56, 4.57, 4.63, 4.64 & 4.66). In XPL subgrain deformation is clear (Figures 4.54, 4.55, 4.58 & 4.59) and quartz grains are elongate parallel to the paleofabric (Figure 4.48), evidencing shear strain post pegmatite formation. As a structurally isotropic mineral, quartz occurs as a polygonal aggregate. However, the occurrence of micas within the matrix, results in the microstructure being dominated by the low-energy faces of the structurally anisotropic micas. Consequently, much of the quartz is texturally pinned, most often by micas oriented parallel to the fabric, as the quartz attempts to achieve its lowest free energy state (Vernon, 2018), and consequently much of the quartz is not polygonal. There is also evidence for the pinning effect inhibiting grain growth, with lesser quartz grain size in matrix that is more enriched in micas (Figures 4.45, 4.46, 4.47 & 4.48).

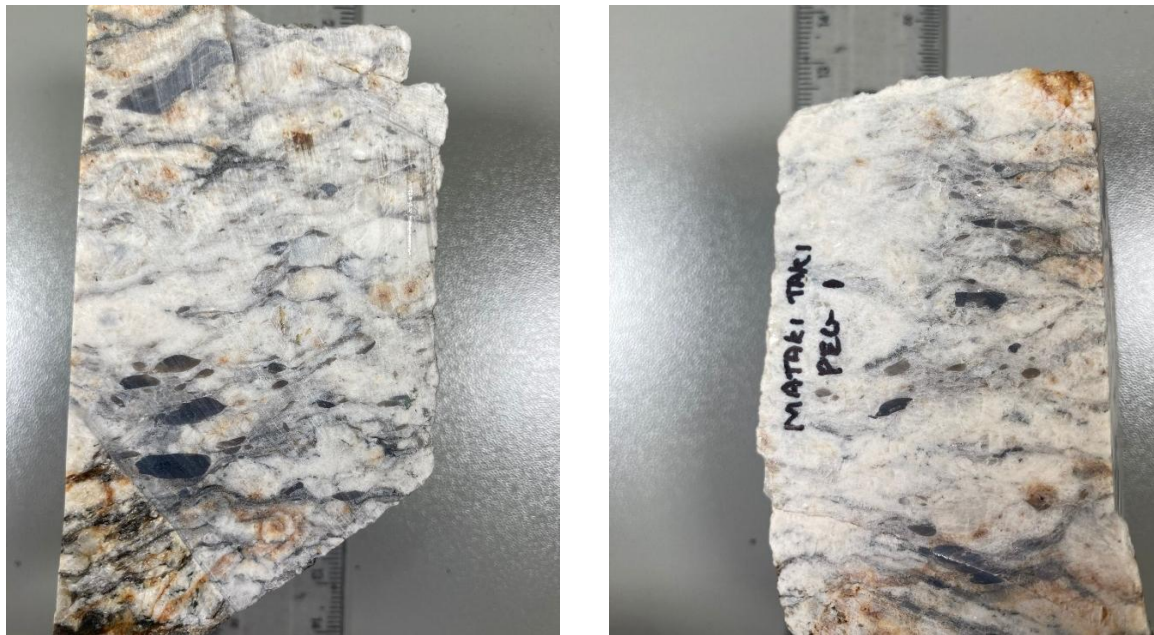


Figure 4.44: Mataketake Pegmatite hand specimen (2MP.1). Quartz and feldspar dominated rock, hence the white appearance. Large mica porphyroblasts appear aligned with the long axis oriented left-right and contrast to the white coloured quartz and feldspar. Deformation has resulted in mica porphyroblasts appearing as 'fish'.

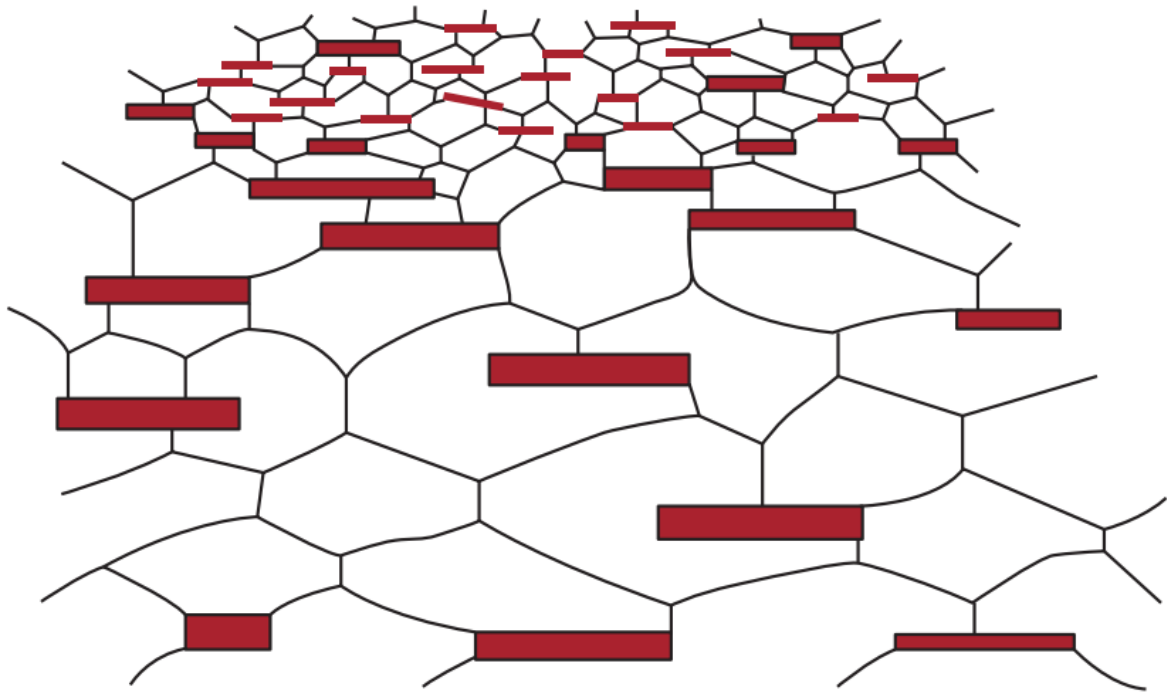


Figure 4.45: From (Vernon, 2018); showing the dominant effect that structurally anisotropic micas (red) can have on a quartz (white) – mica rock. In mica-rich regions, quartz growth is inhibited by mica grains. Quartz-quartz boundaries attach to these mica grains, retarding growth.

The mica ‘streaks’ are comprised of ‘aggregate’ mica grains, with grain shape principally controlled by ‘smearing’ due to shear strain. These micaceous ‘aggregates’ appear cataclastic; with ‘smearing’/fracturing of grains followed by annealing. The annealing process is controlled by crystal faces, with accidents of mutual impingement along the -001 - plane inhibiting growth of adjacent grains. These micaceous streaks anastomose ubiquitously throughout the pegmatites, accentuating the shear-aligned fabric (Figures 4.46, 4.48, 4.52, 4.56, 4.62, 4.63 & 4.64). Within these aggregate ‘streaks’, it is common that fractured grains are aligned (Figure 4.46); however, it is not uncommon for decussate aggregate textures to be observed (Figure 4.61). The observed variation in aligned/decussate textures is attributed to the microstructure of more structurally anisotropic minerals being dominantly controlled by mutual impingement, rather than mutual adjustment; this is due to low-energy forms dominating the microstructure in structurally anisotropic minerals ((Vernon, 1976, 2004).

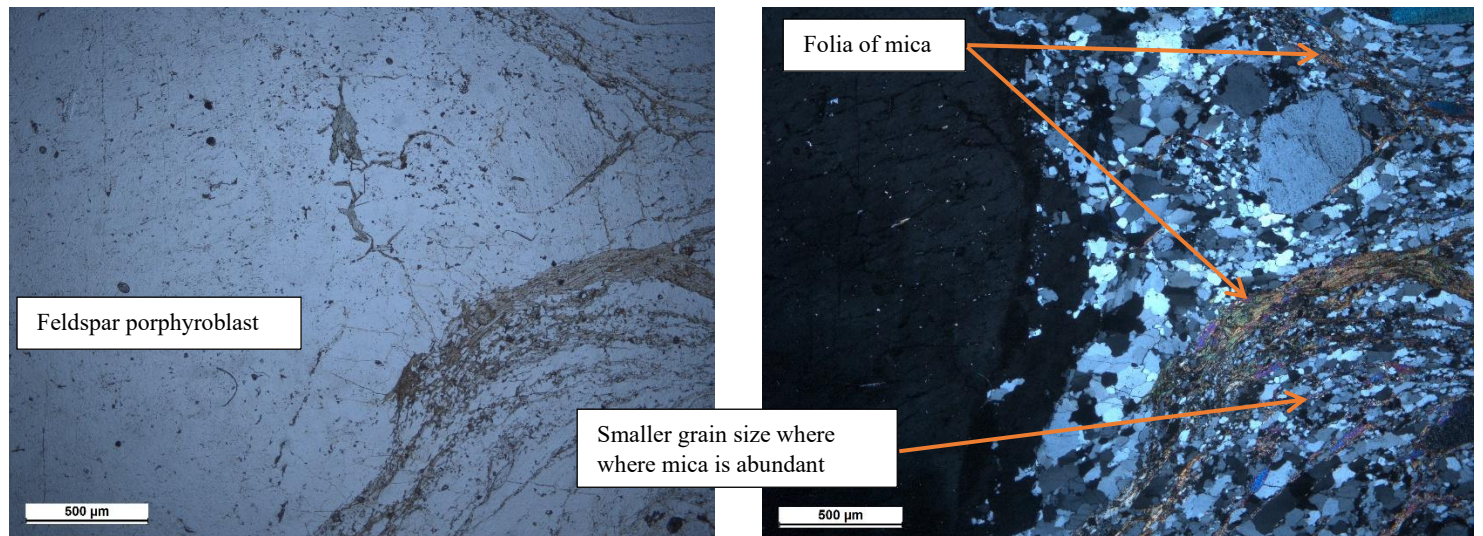


Figure 4.46: 2MP.1 (40µm Section) No.001 – Large feldspar porphyroblast (inclusion textures mentioned later). Image also displays folia of muscovite, that anastomoses around porphyroblasts and grains. Note that where layers of foliated mica are abundant, the size of the polygonal quartzofeldspathic aggregate matrix is reduced – this is because micas are structurally anisotropic and therefore on the 001 plane they attain very low interfacial energies and are super stable, this means they dominate the microstructure. Qtz-qtz and qtz-fsp are inhibited in terms of growth due to the stability of mica on the 001 plane, although these junctions may mobilise, they are immobilised ‘pinned’ once they reach the end of mica grains. The dominance of ‘structurally anisotropic’ micas over the ‘structurally isotropic’ qtz and fsp is a key control in the microstructure seen in the schists (gneisses) and these pegmatites.

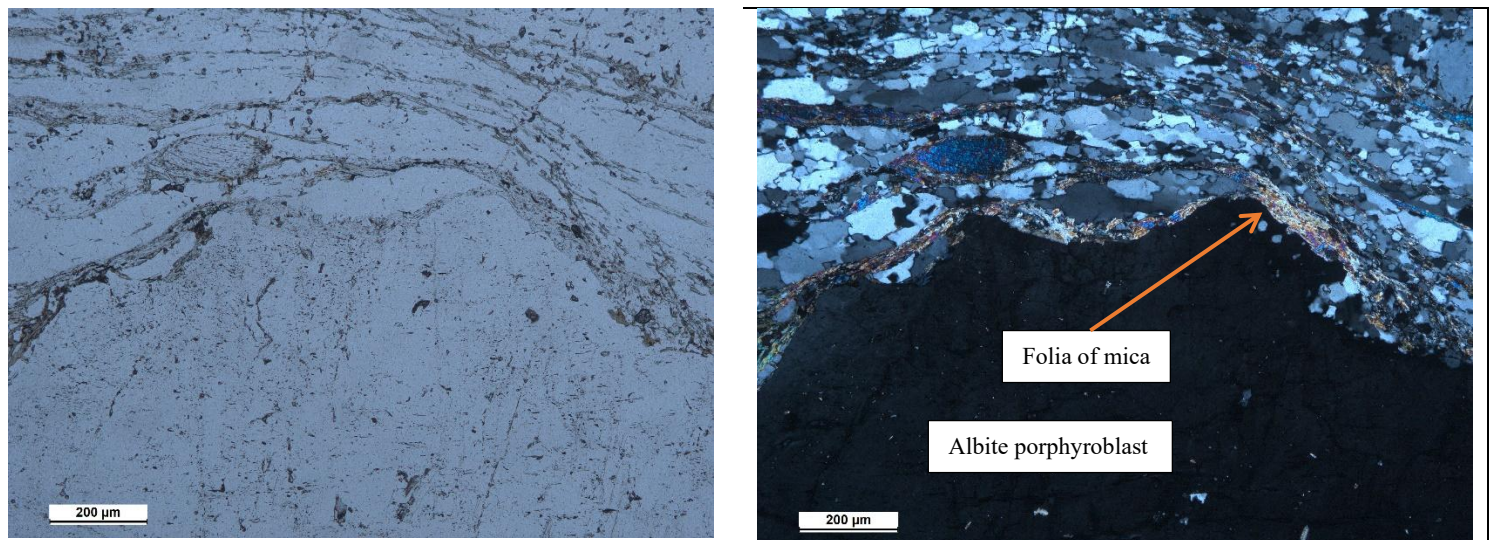


Figure 4.47: 2MP.1 (40µm Section) No.003 – Folia of muscovite and biotite mantle an albite porphyroblast. These anastomosing, finer folia are present throughout pegmatite and schist samples. Another characteristic shown here is the ability for the ‘structurally anisotropic’ micas to ‘elongate’ the quartz grains in the direction of foliation. Note the inclusion of quartz ‘beads’ within the albite (toward the top right of the albite porphyroblast) - this is described later.

Plagioclase is generally albitic in composition, averaging ~An18.1 for analysed compositions (see Chapter 5). Intense deformation has disturbed the original plagioclase phenocrysts, resulting in fractured porphyroblasts (Figures 4.48, 4.49, 4.50, 4.58, 4.59 & 4.66), often with patchy extinction and kink-banding (Figure 4.48, 4.50 & 4.54). Plagioclase porphyroblasts display bookshelf fracturing,

speckled appearances, sericitization and subsolidus growth rims (Figures 4.49, 4.59 & 4.60). These growth rims occur on fractured porphyroblasts and are identified by different birefringence in XPL, an absence of ‘speckles or different greyscale in back-scattered electron images (which evidences distinct atomic weight and therefore distinct compositions). Fractured porphyroblasts are ubiquitous, with fracturing events occurring simultaneously with quartz matrix recrystallisation (Figures 4.48, 4.49, 4.50, 4.58, 4.59 & 4.68). Fractures are commonly infilled with quartz, formed via solution-precipitation creep (fluid assisted mass transfer), which can manifest as the only unstrained quartz in the sample.

Feldspar rims commonly contain trails of inclusions, or ‘beads’ of quartz (Figures 4.47, 4.55, 4.61, 4.67, 4.69, 4.70). This can happen due to varying reasons. Subgrain deformation is a real possibility (whereby precipitating quartz develops lattice dislocations due to strain, or variances in stored energy between neighbouring grains results in grain boundary migration (Vernon, 2018)), or heightened strain has enhanced nucleation rate, resulting in numerous quartz grains forming along fractures (Rushmer, 1996). Holness and Sawyer (2008) highlight how a reduction in cooling rate may result in aggregated super-solidus “equigranular and equant” quartz and feldspar grains along quartz-feldspar grain boundaries, also known as the “string of beads” texture (Holness & Isherwood, 2003; Holness & Sawyer, 2008). Alternatively, irregular quartz-feldspar grain boundaries may occur due to a reduction in cooling rate (Holness & Sawyer, 2008). Isolated strings of beads are highly disequilibrium features, which Holness and Clemens (1999) attribute to a crystallised melt phase dividing into lower energy forms. Due to the proto-mylonitic texture, which evidences post-emplacement shear, we attribute the observed “string of beads” texture to the nucleation rate being enhanced by strain, and/or a reduction in cooling rate. Importantly, this texture communicates disequilibrium, which is particularly concerned with the rims of feldspar grains (where the “string of beads” texture is located).

Briggs and Cottle (2018) report finding K-feldspar in samples of the Mataketake Pegmatites. (Dyck et al., 2020) highlight differing reactions for fluid-present and fluid-absent melting of a metasediment and show how the products of these reactions can vary. In vapour-absent settings K-feldspar can precipitate as a peritectic phase (Dyck et al., 2020). Conversely, in vapour-present reactions, K-feldspar is solely produced via melt crystallisation (Dyck et al., 2020). This means that the presence or absence of K-feldspar in the samples could be an important petrogenetic marker. However, K-feldspar was not observed in any analysed samples of this study. We searched for associated microstructures (Dyck et al., 2020), which may have indicated that K-feldspar was at one point present, but these were not present. String of beads are also observed by Dyck et al. (2020) along K-feldspar-plagioclase boundaries, where a myrmekite also forms. As such, we looked closely at all string of bead textures, to see if myrmekite is also present. Myrmekitic textures may have evidenced K-feldspar presence at an earlier stage, however none were found.

There is no evidence for melt precipitated quartz (primary quartz). Sericitization and the ‘muddy’ texture of plagioclase may be attributed to hydrothermal metasomatism Rong and Wang (2016). Rong and Wang (2016) highlight how the development of micropores, which result in the speckled appearance (Figures 4.49, 4.50, 4.54, 4.55, 4.58, 4.59, 4.60, 4.64, 4.66 & 4.68), through reaction with hydrothermal fluids, is thought to be linked to sericitization, and plays a contributing role in co-oriented albitization. Decomposition of plagioclase, through the infiltration of hydrothermal fluids into micropores, results in the removal of CaO, whilst a residuum of Na₂O, Al₂O₃, and SiO₂ remains. This facilitates sericite formation in micropores, as K₂O and H₂O in fluids combine with Al₂O₃ and SiO₂, locally replacing plagioclase (Rong & Wang 2016).

Textural observations point to a relatively high-temperature (relative to metamorphic temperatures) pegmatite intrusion, followed by moderate strain, resulting in protomylonitic texture, with extensive subgrain deformation of quartz, and slip along mica cleavage plains. Principally, deformation overprint is evidence by most new growth being quartz, with lesser feldspar growth. Adjacent to porphyroblasts, pressure shadows are observed, with quartz dominating mineralogy in these zones. Evidence for post-magmatic hydrothermal metasomatism is debatable; the speckled, ‘muddy’ appearance of plagioclase, with sericitization occasionally visible in porphyroblasts (Rong & Wang, 2016).

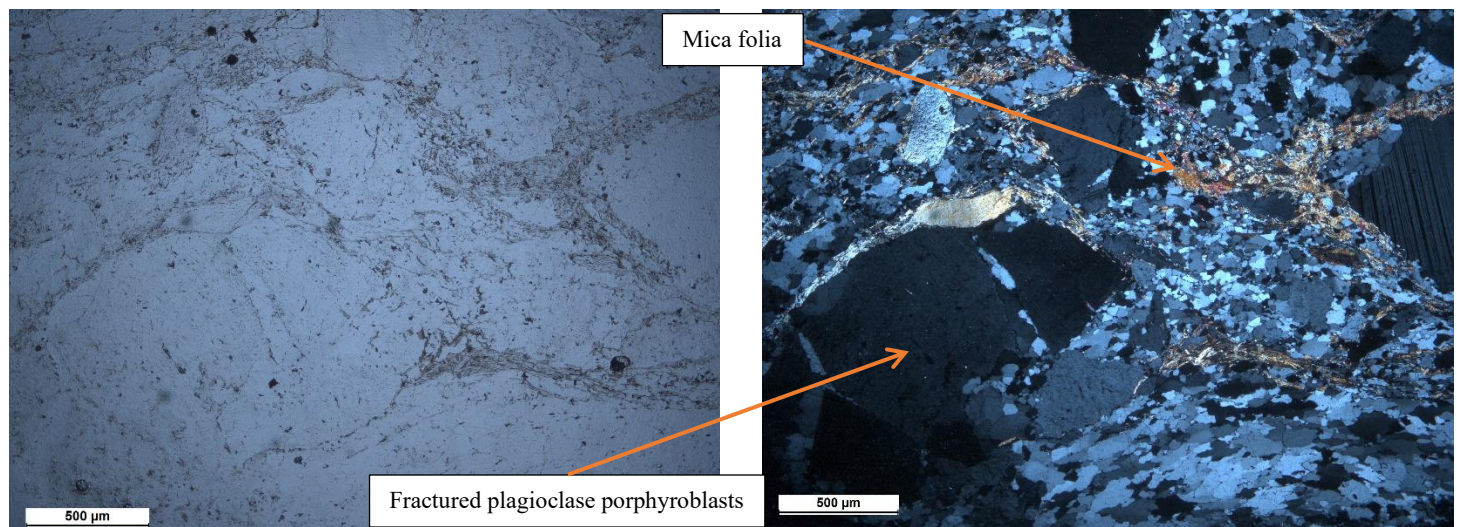


Figure 4.48: 2MP.1 (40μm Section) No.005 – These thin section photomicrographs display many of the key textures: anastomosing mica folia, bookshelf fracturing of plagioclase porphyroblasts, subgrain deformation of quartz, quartz recrystallising in feldspar fractures, variation in quartzofeldspathic grain size due to textural pinning, patchy extinction within feldspar porphyroblasts due to strain-induced lattice disorientation, and deformation twinning is observed in the feldspar porphyroblasts on the right.

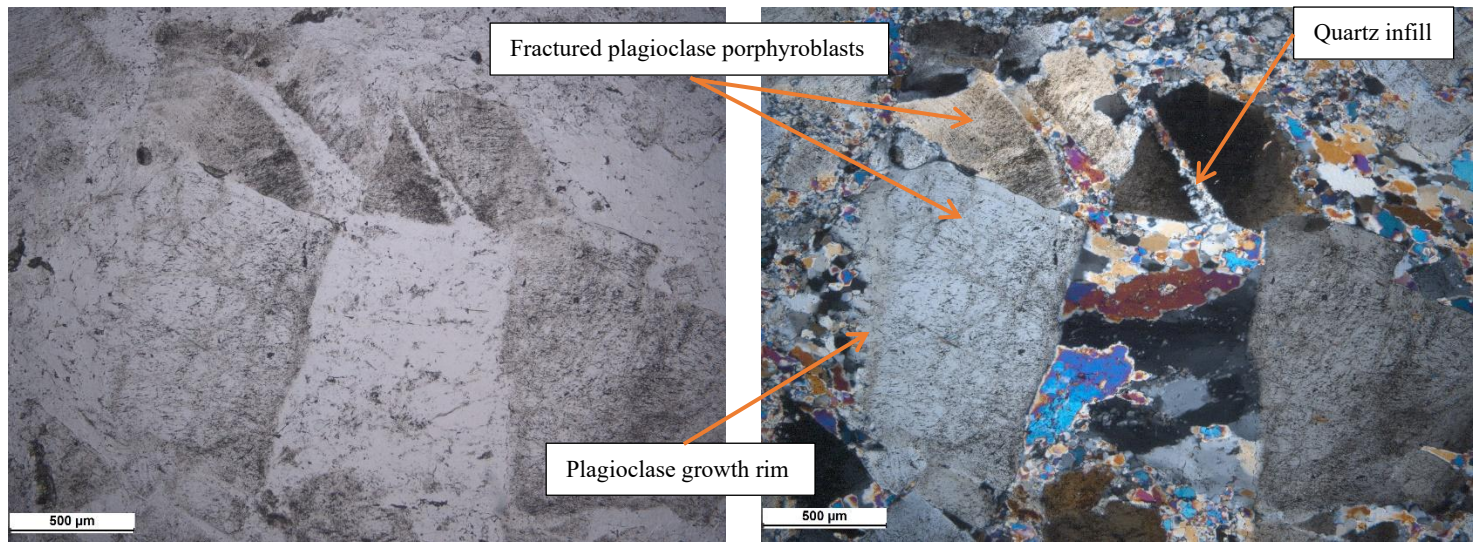
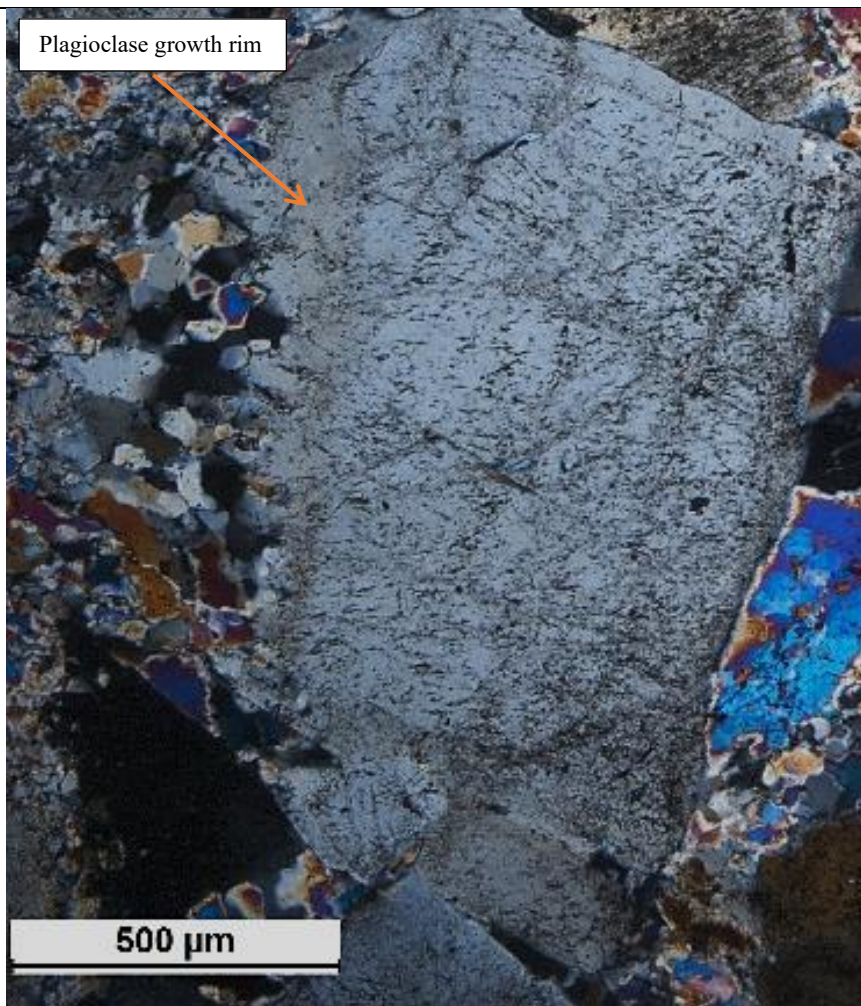


Figure 4.49: 2MP.1.02 (80μm section) – Fractured plagioclase porphyroblast(s), with quartz infilling the fractures. Disequilibrium textures are also visible in the plagioclase. Plagioclase growth rim is clear on the left and top of the centre-left 'book'; this is better observed in 2MP.1.04. Quartz-dominated matrix and infill shows lots of subgrain deformation. The image below shows a close-up of feldspar growth rims; note the separate colour for the feldspar on the left margin of the porphyroblast.



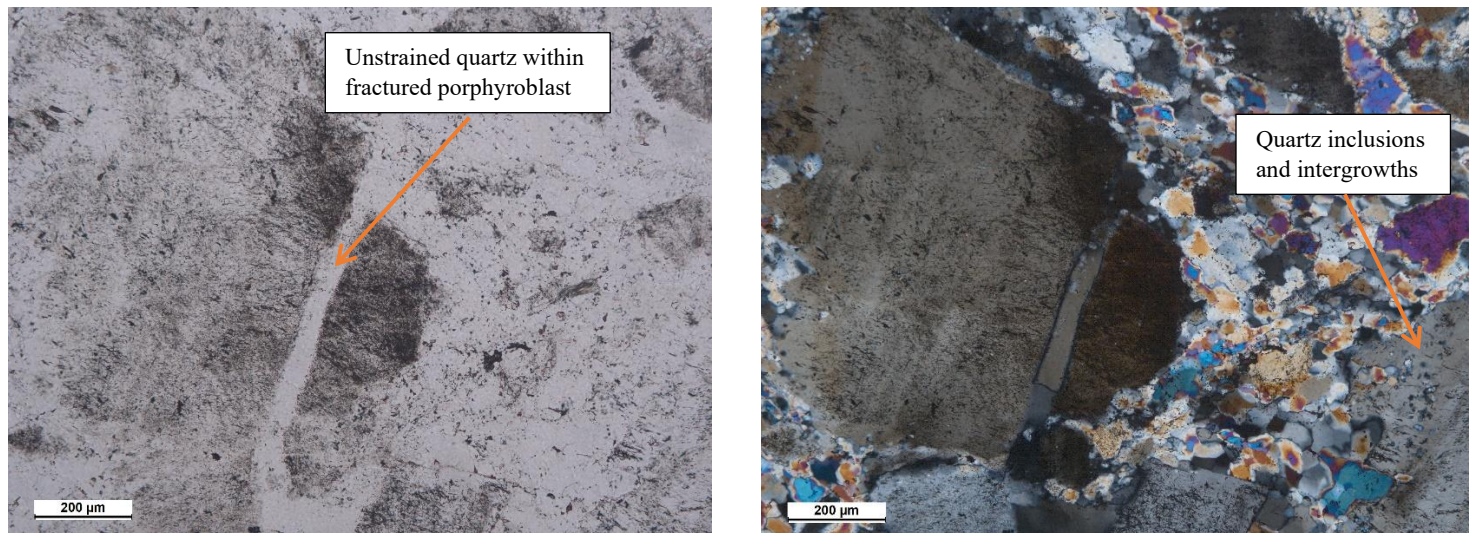


Figure 4.50: 2MP.1.07 (80µm section) – A muddy plagioclase porphyroblast, which indicates alteration. Plagioclase is fractured and unstrained quartz has precipitated in the fracture. Outside the quartz-dominated matrix shows lots of subgrain deformation. Disequilibrium textures are also visible in the plagioclase on the right – which contains inclusions and intergrowths with quartz. The existence of unstrained quartz within fractured porphyroblasts reveals recrystallisation at a later stage. PPL shows the ‘muddy’ texture within plagioclase, which we interpret as a product of alteration. XPL shows distinct parts of the plagioclase grains going into extinction at different points of rotation, notably the right side of this porphyroblast heads into extinction together. This is also where the grain is fractured and where it appears most “murky”; possibly indicating the right side of this grain was deformed to greater extent by shear strain than the rest.

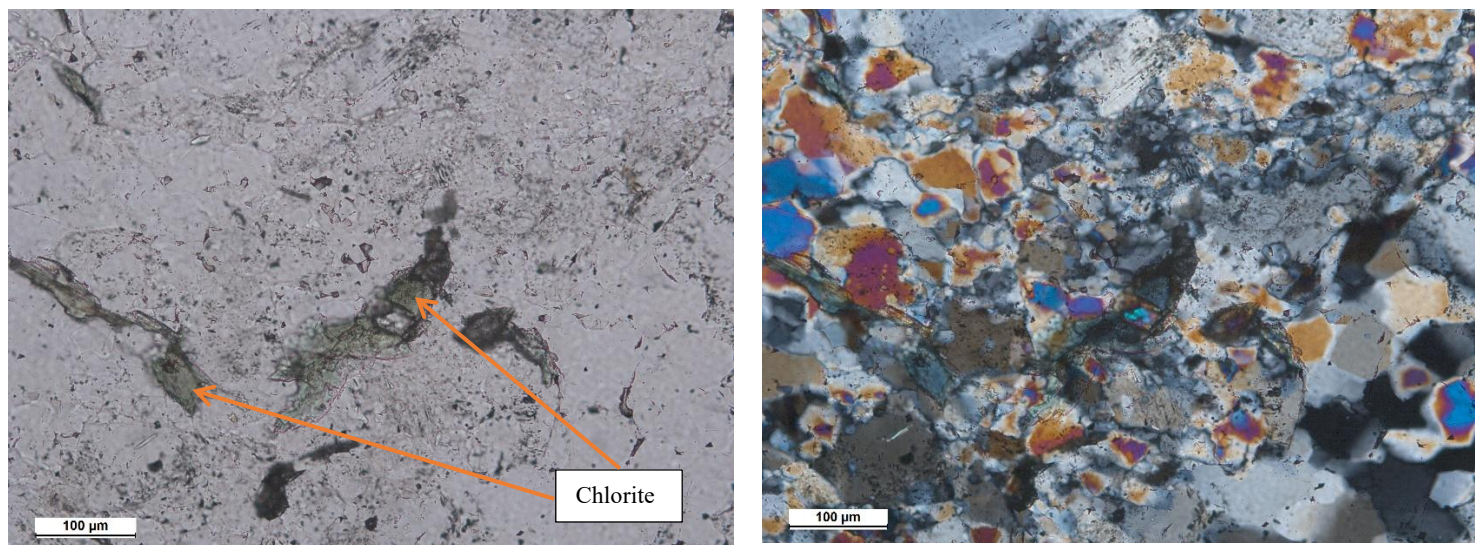


Figure 4.51: 2MP.1.05 (80µm section) – Chlorite grains in pegmatite, surrounded by quartzofeldspathic grains. The murky grain(s) to the top right are feldspar.

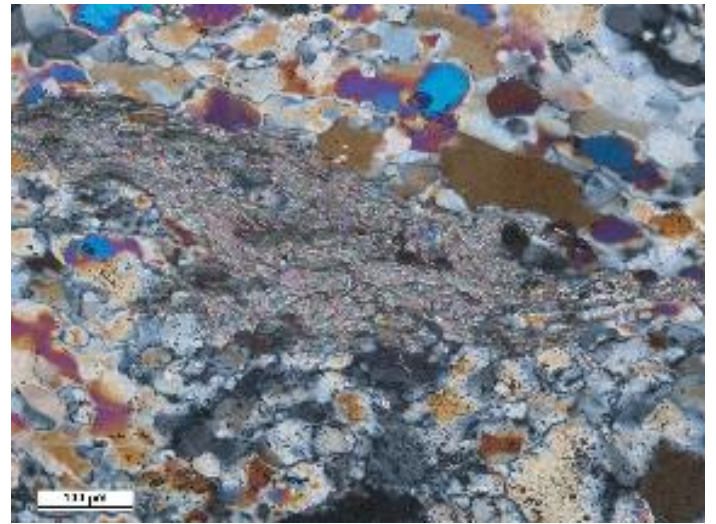
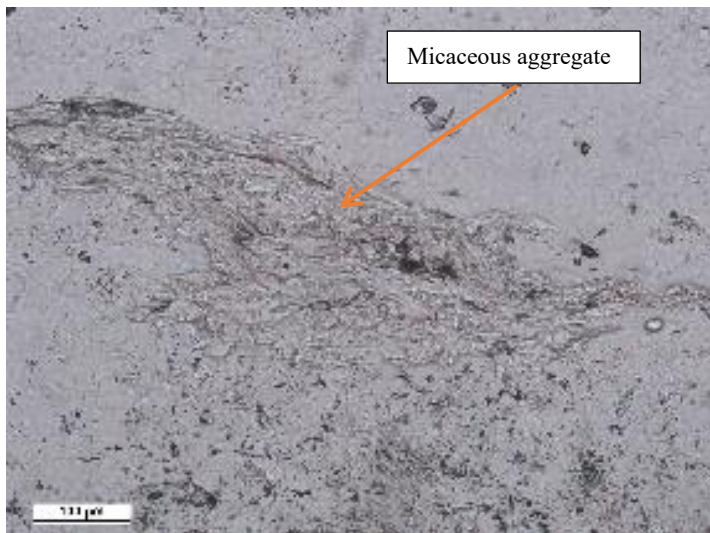


Figure 4.52: 2MP.1.08 (80μm section) – A micaceous aggregate consisting generally of muscovite intrudes through a quartz-dominated matrix region. Generally, the fine ‘flakes’ of muscovite are paleofabric oriented – although some appear more random. This texture is attributed to ‘slippage’ along muscovite cleavage planes due to shear strain. These aggregates are ubiquitous through the pegmatite sections and appear as anastomosing streaks.

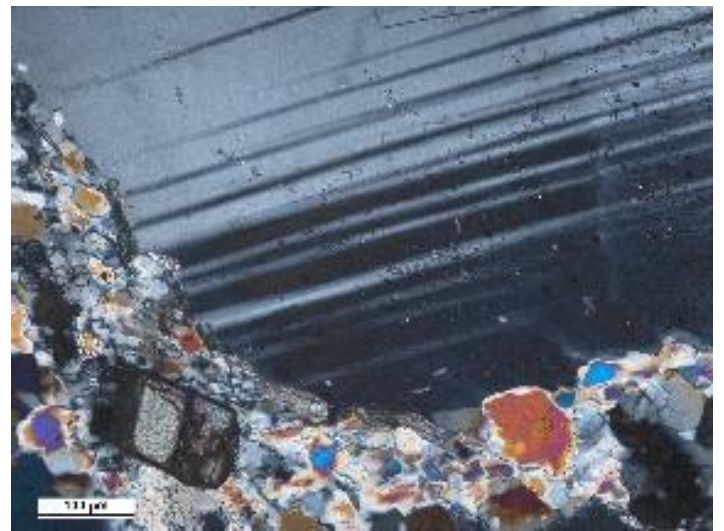
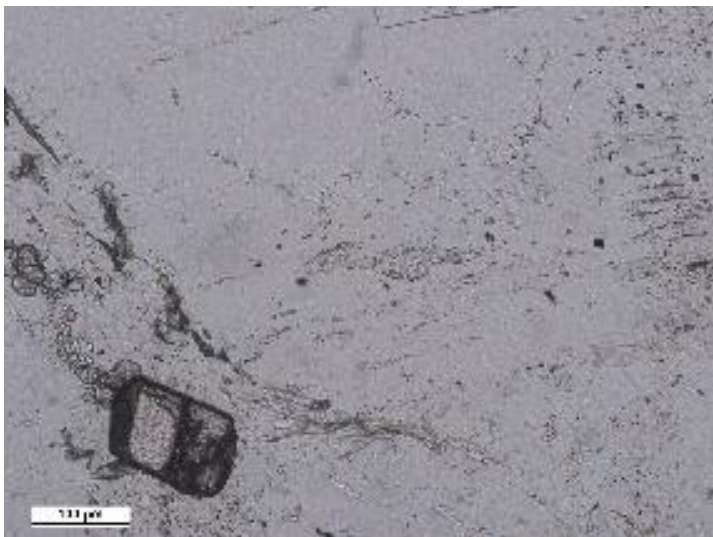


Figure 4.53: 2MP.1.10 (80μm section) – plagioclase porphyroblast displaying twinning. PPL displays a slight ‘muddy’ appearance of the plagioclase, likely due to onset of alteration. Sericitization has then occurred – this is thought to be linked to the appearance of micropores – reaction with hydrothermal fluid mean micropores formed – allowing for sericitization to occur. To the bottom left of the porphyroblast, flakes of muscovite are ‘smeared’ along the boundary. The matrix is quartz and feldspar dominated, with the speckles being characteristic of plagioclase in these pegmatites. A grain of zircon can clearly be seen (lower left).

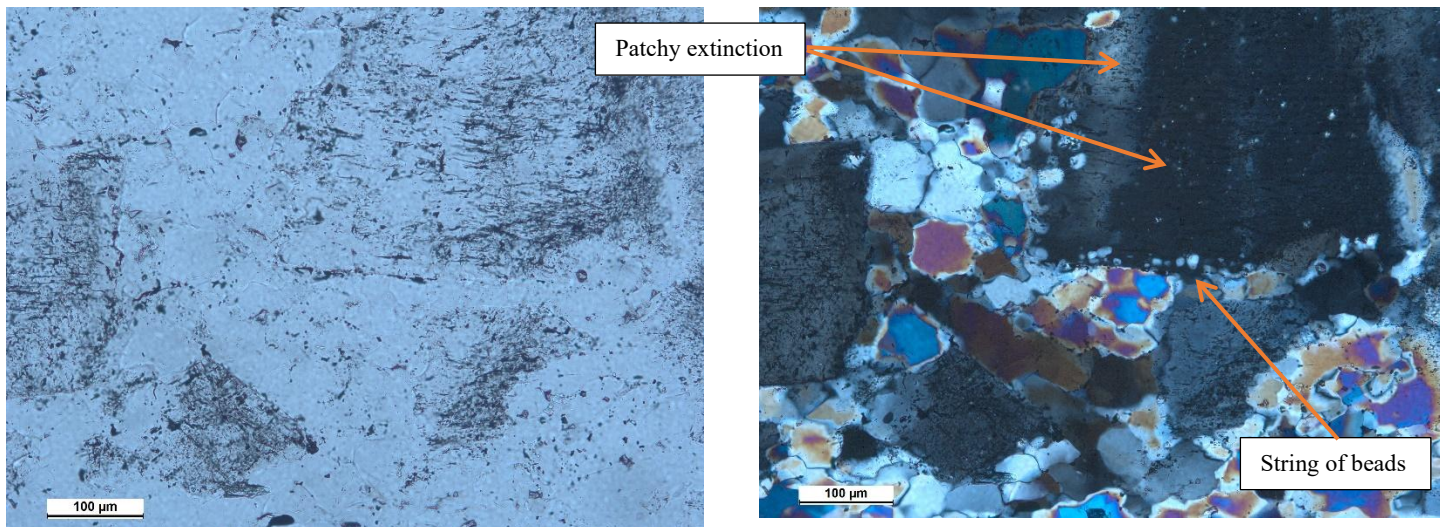


Figure 4.54: 2MP.1.17 (80µm section) – feldspar grains, with patchy extinction due to lattice misorientation. Speckled appearance is due to microfracturing of feldspar grains and infill. Quartz grains in matrix show extensive subgrain deformation. This image shows the 'string of beads' textures very well (lower boundary of feldspar grain, centre of image).

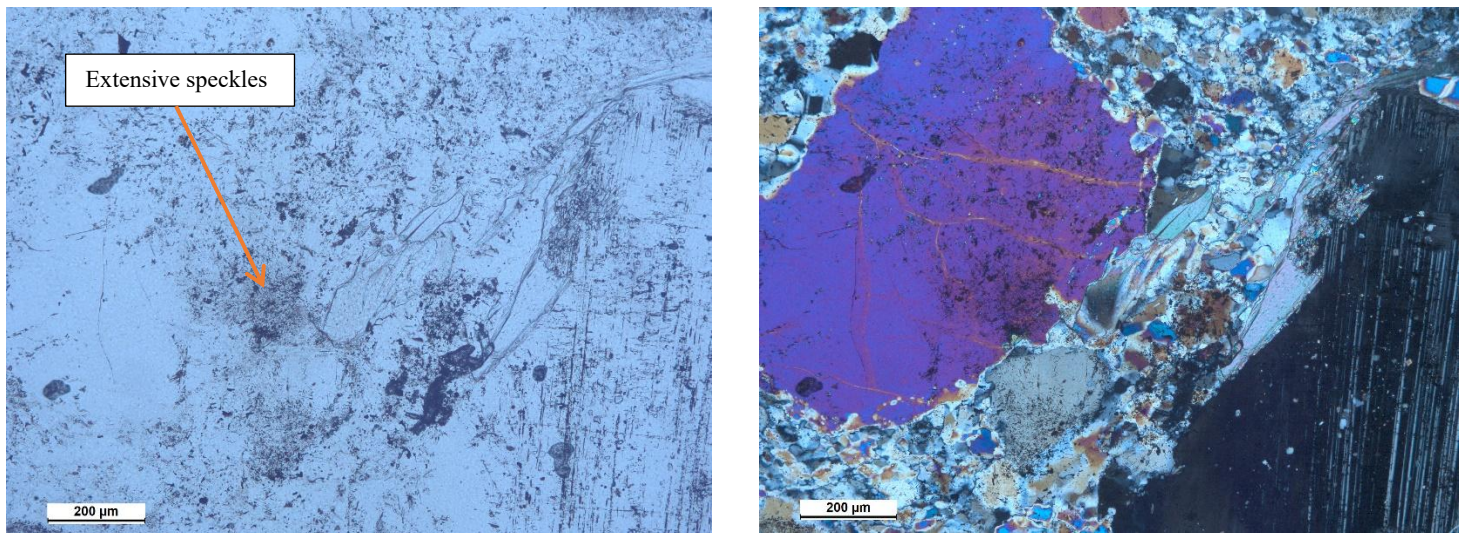


Figure 4.55: 2MP.1.20 (80µm section) – PPL shows extensive speckles within feldspar grains. Note how one portion of the feldspar porphyroblasts on the left contains a lack of speckles/inclusions. We interpret this as due to lesser lattice deformation via strain relative to the rest of the porphyroblast. The feldspar porphyroblasts on the right shows clear deformation twinning. There are extensive inclusions in the porphyroblast on the right. Intense deformation of muscovite grains has resulted in significant 'smearing'. Within the quartzofeldspathic matrix, grain boundaries are difficult to make out, due to extensive subgrain deformation and more importantly due to this section being thick at 80µm.

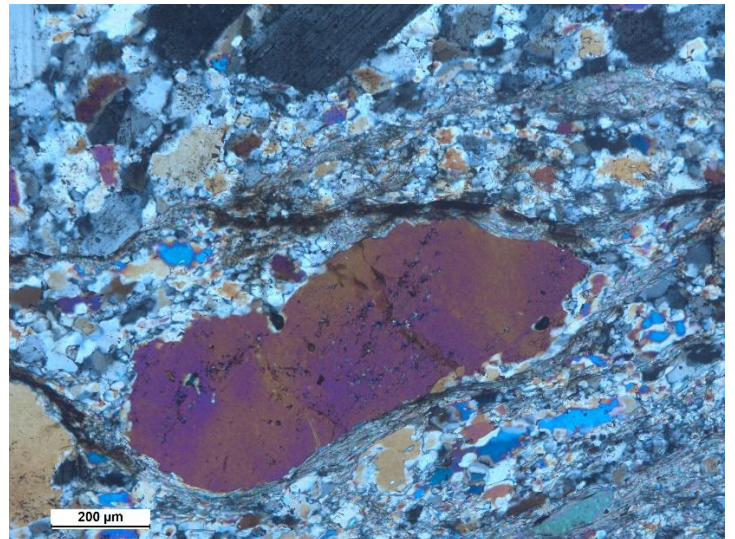
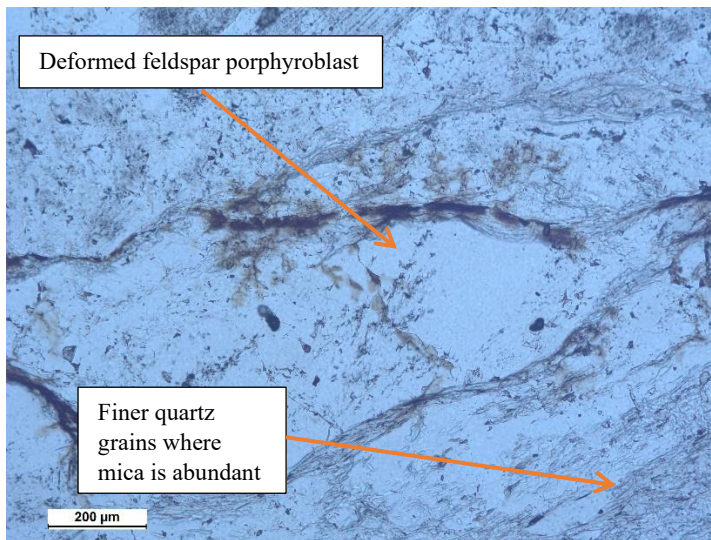


Figure 4.56: 2MP.1.23 (80μm section) – A deformed feldspar porphyroblast with anastomosing mica outlining the wider region. The presence of biotite highlights the aggregate micas, and more generally outlines the wider pressure region associated with the deformation. Note the inclusions within the plagioclase, possibly due to sericitization. Matrix quartz grains are confined in size due to textural pinning through fine mica grains.

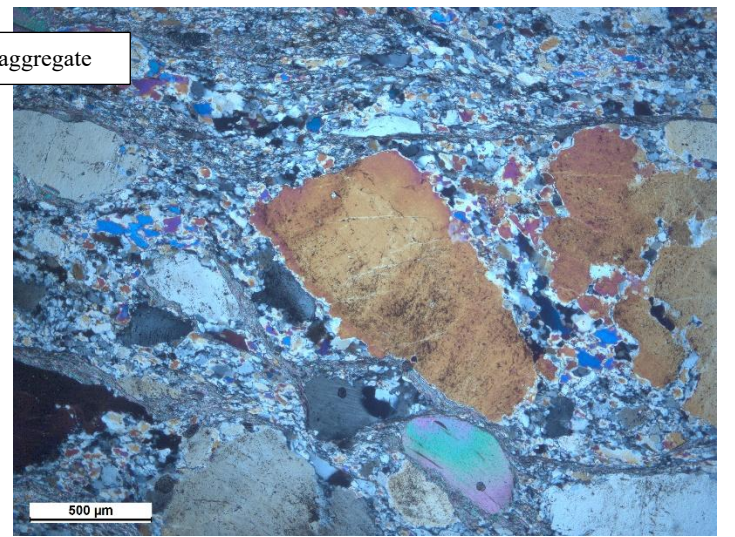
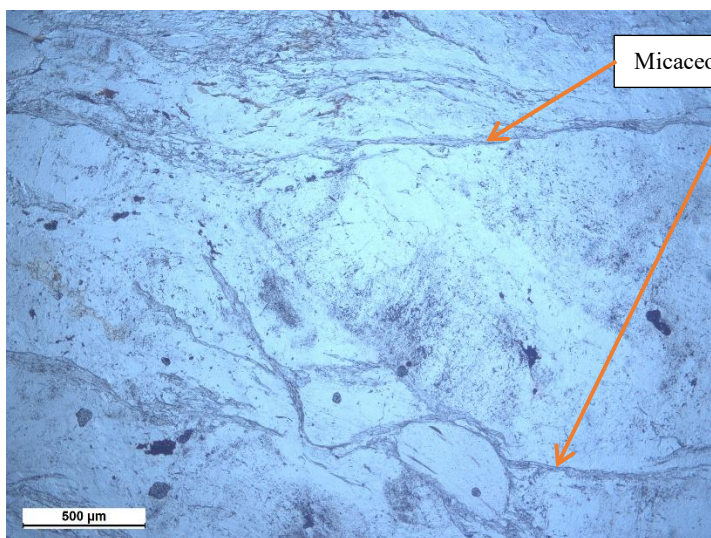


Figure 4.57: 2MP.1.24 (80μm section) – A high level view of the protomylonitic texture. Note the fractured porphyroblast on the right; the micaceous aggregate outlines the extent to its original size before fracturing, embrittlement, and recrystallisation. This image displays the ‘smeared’ micas very well. Deformation twins observed within the feldspar grain to the left of the muscovite porphyroblast.

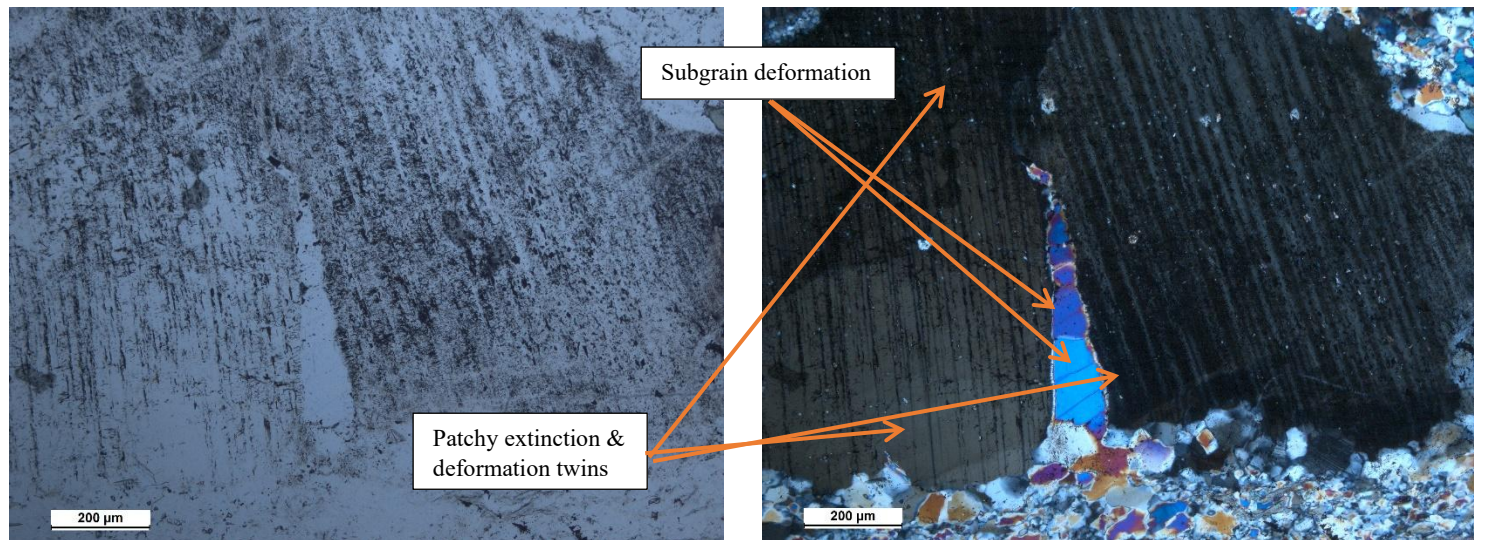


Figure 4.58: 2MP.1.26 (80μm section) – Bookshelf fractured plagioclase porphyroblast, with quartz crystallising in the fracture. Often quartz is unstrained when crystallising within fractures, but this quartz shows subgrain deformation and even fractures, indicating strain event(s) were sustained. Deformation twins are clear, with extensive inclusions. Patchy extinction in porphyroblast due to deformation.

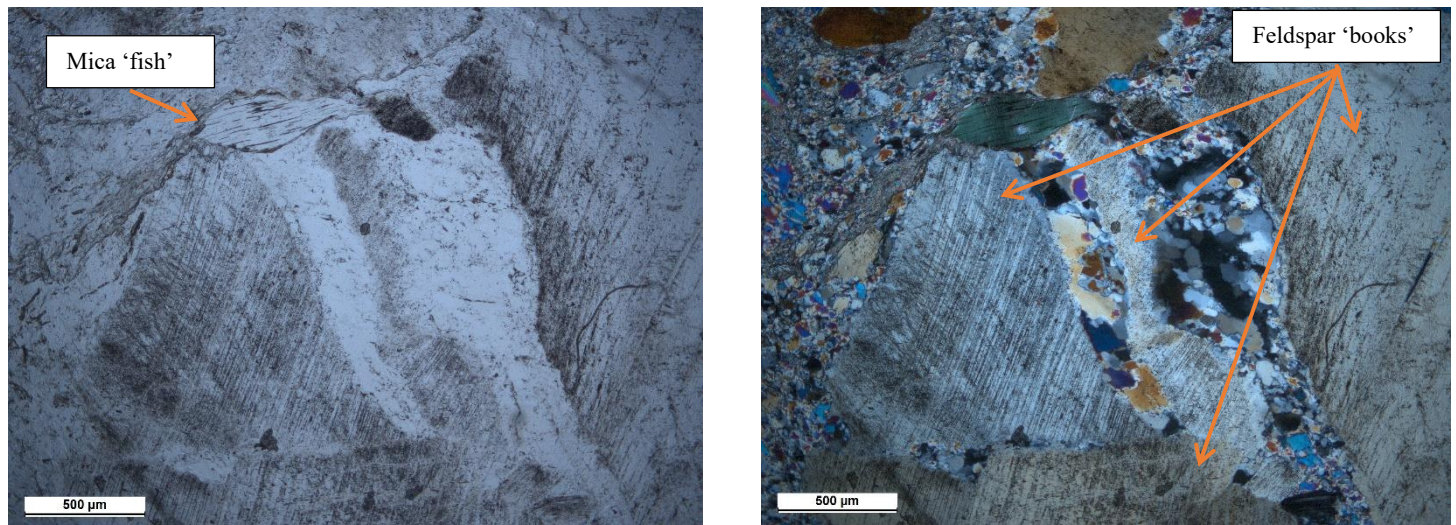


Figure 4.59: 2MP.1.34 (80μm section) – A large feldspar porphyroblast showing bookshelf fracturing. The protolithic feldspar grain must have been very large, evidencing the classic pegmatite texture that will have once existed. Deformation twins within feldspar appear at different angles for separate feldspar 'books', indicating sustained deformation. Quartz-dominated infill between fractures has undergone extensive subgrain deformation. Growth rims are clear on the feldspar books; see the right border of the feldspar 'book' in the mid-left (2MP.1.35 shows this). PPL shows the murky aesthetic of feldspars, indicating deformation and possibly alteration. A muscovite 'fish' is observed in the upper mid-centre of the image, directly above a fracture seam. The image below shows a close up of the feldspar growth rims.

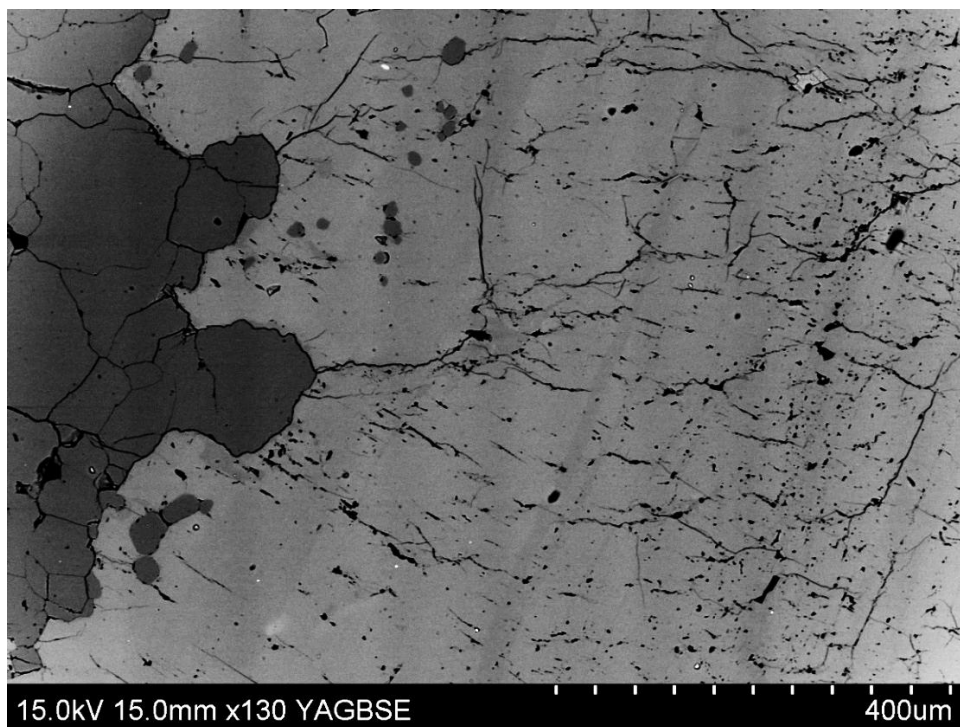
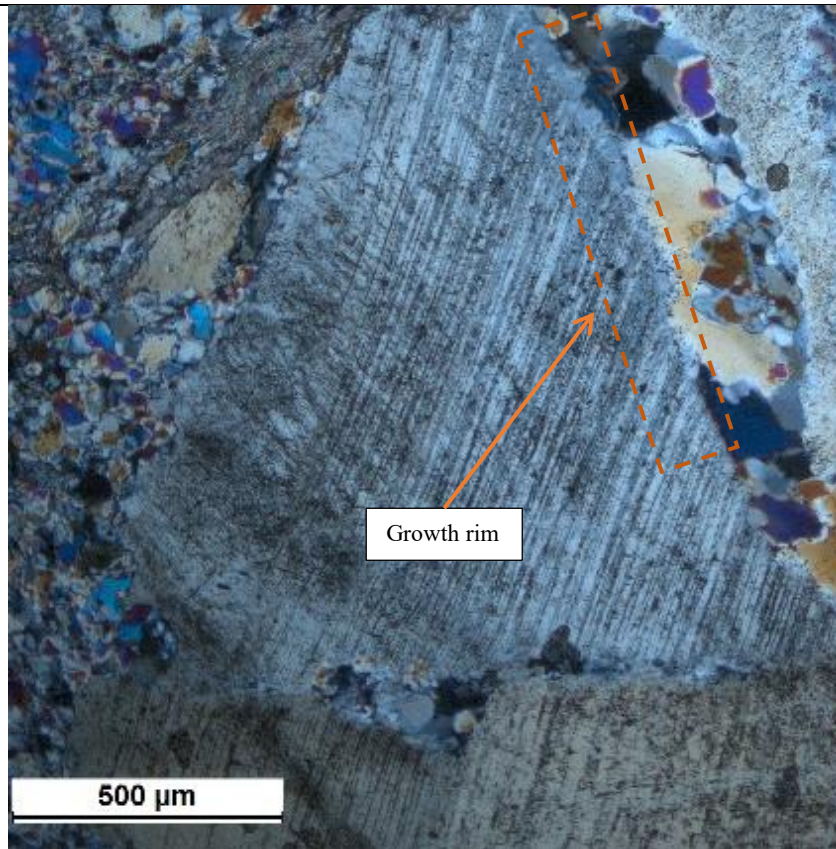


Figure 4.60: Back-scattered electron Image of Mataketake Pegmatite (2MP.1.007). A plagioclase porphyroblast (right) and matrix quartz (left). Note the boundary texture between plagioclase and quartz. Plagioclase on the rim (left of grain) of the porphyroblast does not contain as many inclusions/speckles as the central part does. It also attains an ever-so-slightly darker greyscale. Within this, quartz occurs as 'strings of beads' (Holness, 2018; Holness & Sawyer, 2008).

S1(B) MP.10

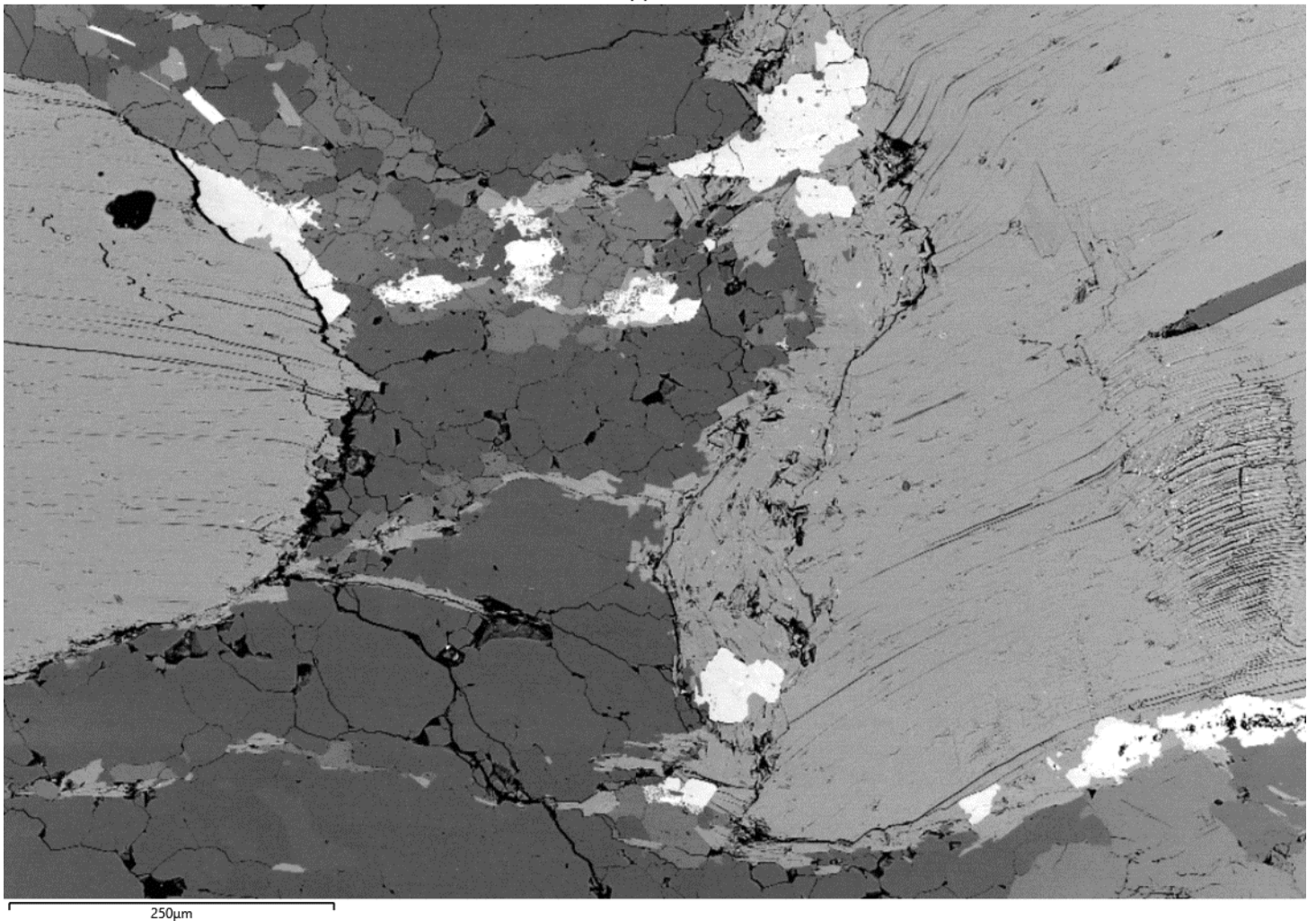


Figure 4.61: 1(B)MP – Back-scattered electron Image (No.10); Black = Holes. Dark grey = quartz, medium-dark grey = albite, light grey = muscovite, grey-white = epidote. Two deformed muscovite porphyroblasts (L&R). Deformation is intense as indicated by: 1) the fractured porphyroblasts, 2) the deformation along muscovite cleavages, 3) the precipitation of intragrain quartz, and 4) the decussate aggregate texture of muscovite ‘flakes’ on the left of the porphyroblast on the right. In-between the two fractured porphyroblasts are quartz, albite (oligoclase) and epidote. Note the pervasive fracturing within the quartzofeldspathic matrix, indicating deformation and recrystallisation.

S1(B) MP.12

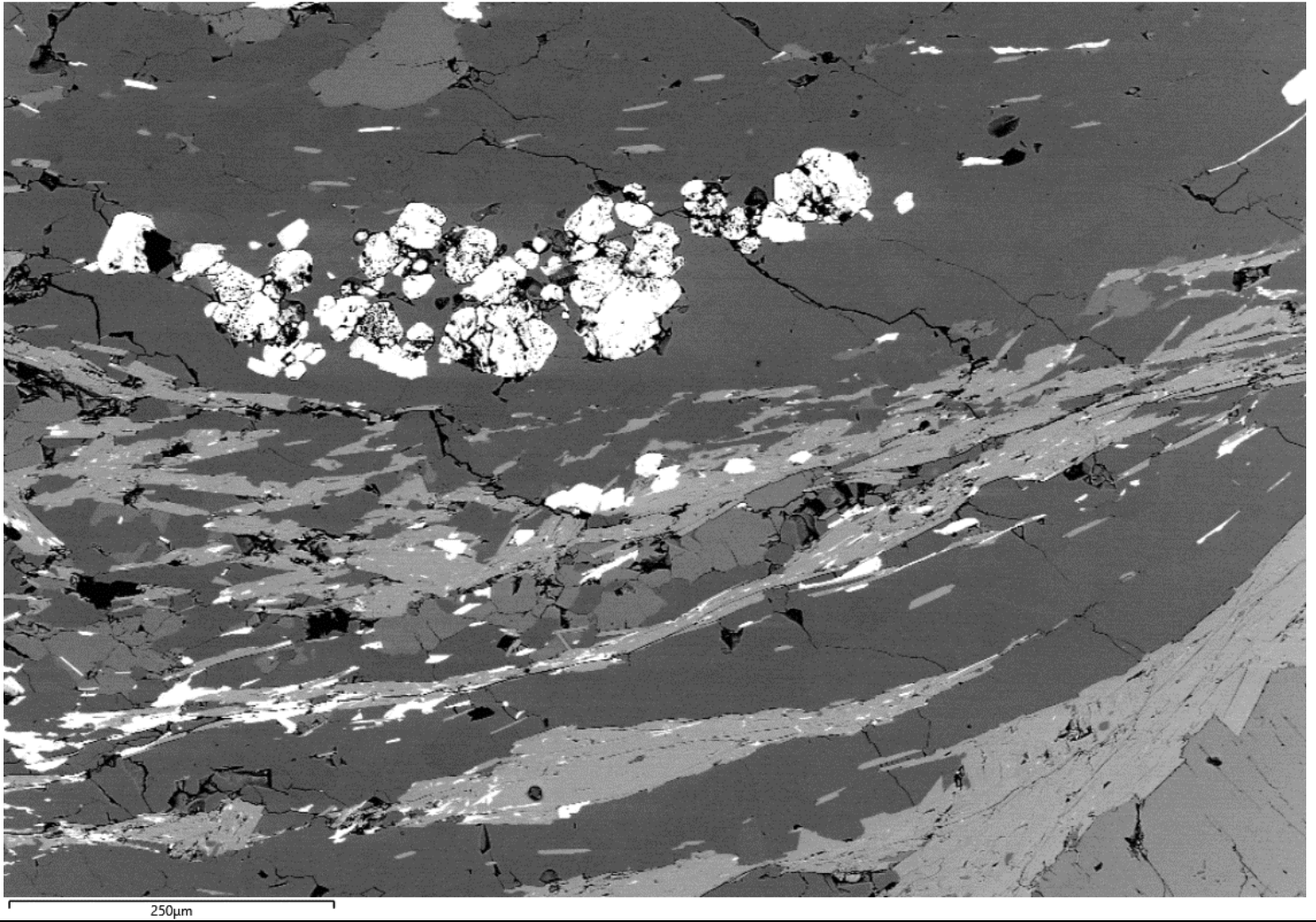


Figure 4.62: 1(B)MP – Back-scattered electron Image (No.12); Black = Holes. Dark grey = quartz, medium-dark grey = albite, light grey = muscovite, white = biotite, titanite, and apatite. Amongst the phase that appear white, the habit of these minerals is the key distinguisher. The biotite occurs as relatively elongate (high long axis:short axis ratio) flakes oriented parallel to the fabric, often within the micaceous streaks, although some are seen above the cluster of rounded white grains, within the quartz matrix. Titanite is similar in its' occurrence, situating itself amongst the muscovite aggregates, however these grains are not as elongate, and appear 'bulkier'. Finally, the apatite grains appear as a cluster of subhedral grains. These grains occur in the upper section of this electron image, and look murky/speckled due to the quantity of holes. This electron image shows the aggregate micaceous streaks very well. It communicates how despite both muscovite and biotite being relatively common in the pegmatite samples, finding grains of sufficient size to conduct Laser-ICP-MS analyses on is difficult. Note how the aggregate micaceous streaks are oriented; they follow the outline of the plagioclase grain on the bottom right. The mica 'aggregate' is dominated by muscovite, and generally the grains are aligned to the fabric, however in some instances the grains appear relatively decussate. See the following image for this electron image in its wider context.

S1(B) MP9 (Area 2)

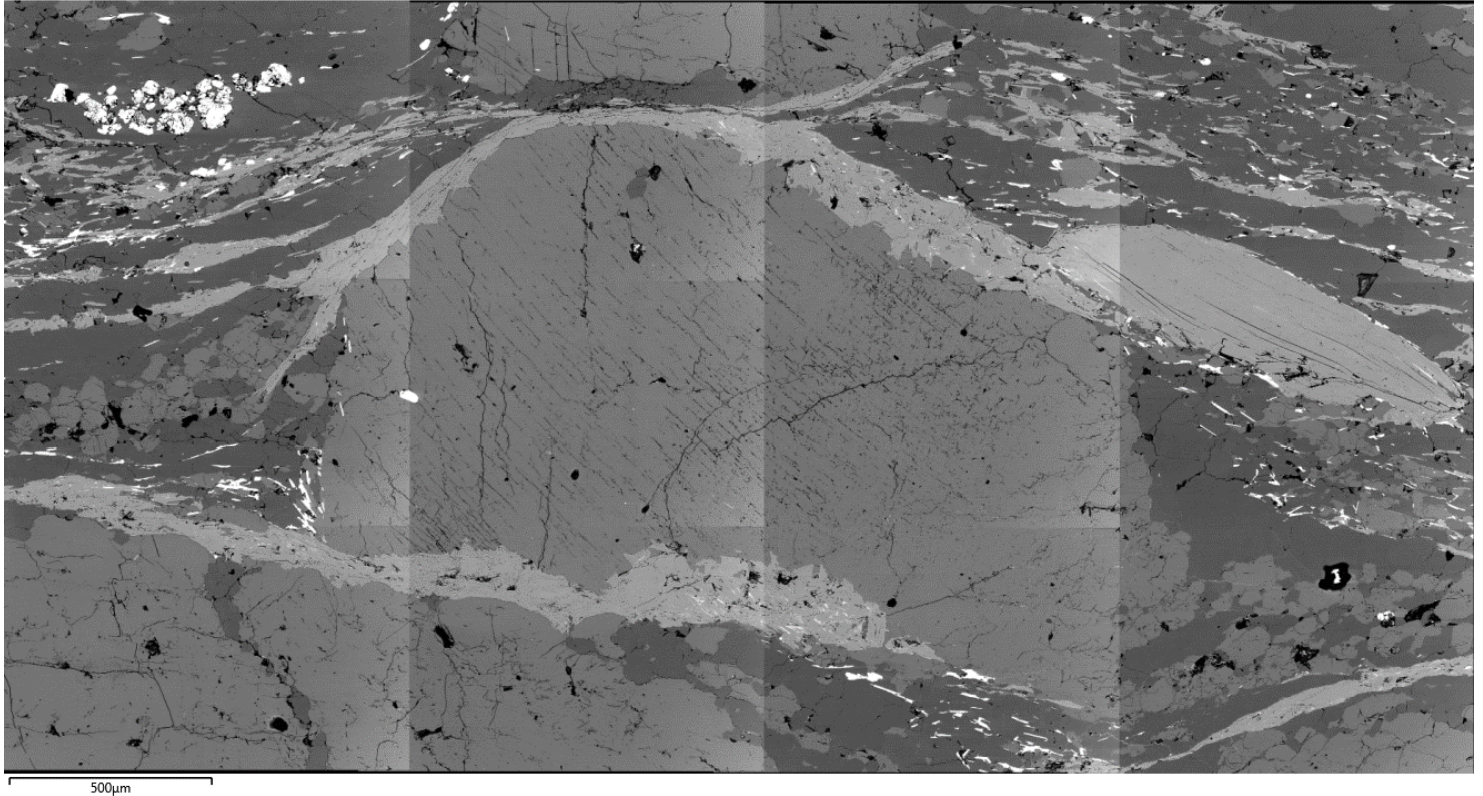


Figure 4.63: 1(B)MP – Montaged Back-scattered Electron Images (No.9), putting the above electron image into context. Black = Holes. Dark grey = quartz, medium-dark grey = albite, light grey = muscovite, white = biotite, titanite, and apatite. In the centre is a plagioclase porphyroblast, with two more located at the bottom left and centre-top. The central porphyroblast measures $\sim 2000\mu\text{m}$ along its' longest axis. As pointed out in Figure X, the micaceous aggregate wraps around the plagioclase porphyroblast. The sheared micas are generally oriented with the fabric, however occasionally mica 'flakes' appear randomly oriented (e.g., the bottom of the central plagioclase porphyroblast). Deformation is intense, with the plagioclase porphyroblast on the bottom left being fractured. Quartz has precipitated within this fracture. Within the pressure shadows of the plagioclase porphyroblasts, quartz has precipitated, along with feldspar grains. We interpret the feldspar grains as remnant fragments of the larger porphyroblasts that have been displaced due to shear strain.

S1(B)MP.6&8 (Area 1)

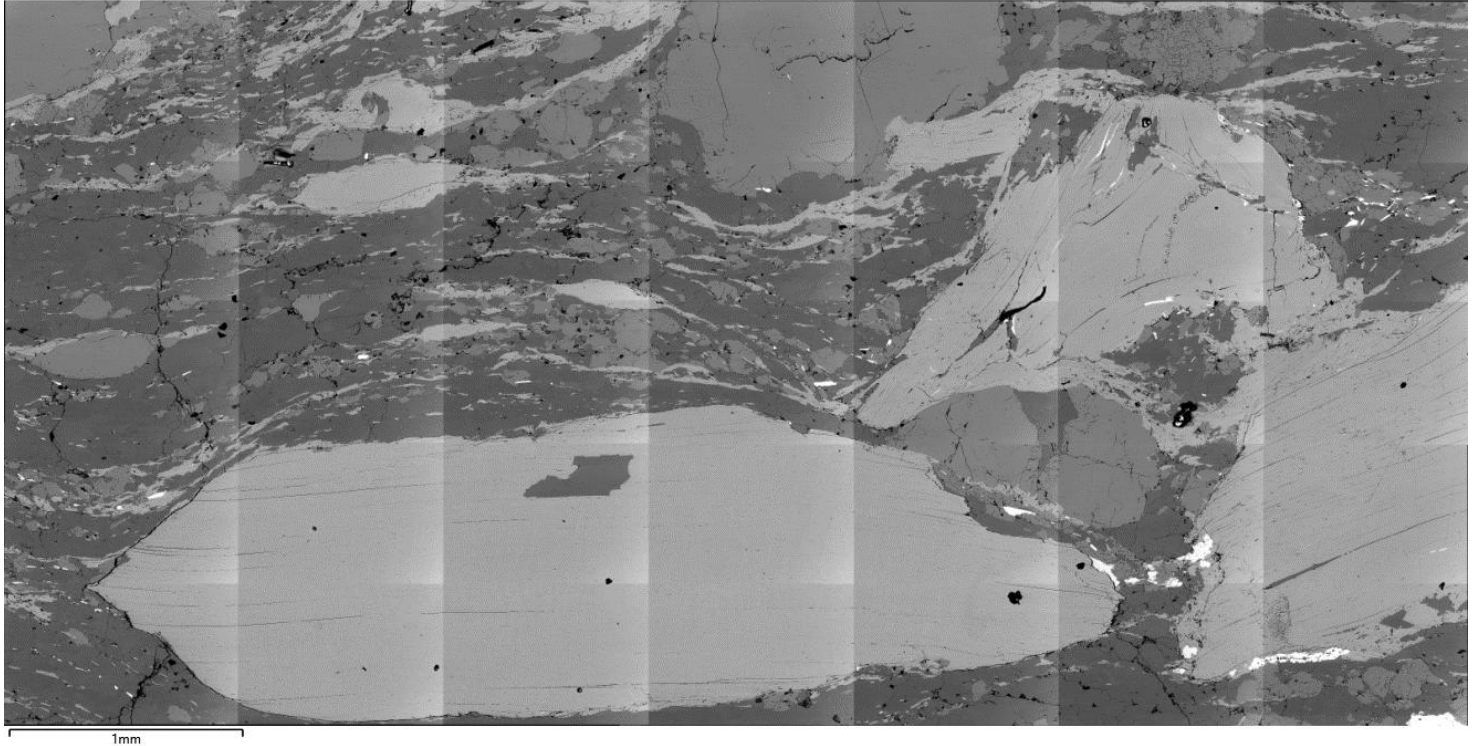


Figure 4.64: 1(B)MP – Montaged back-scattered Electron Image (No.6&8; Area 1); Black = Holes. Dark grey = quartz, medium-dark grey = albite, light grey = muscovite, grey-white = epidote, white = biotite, titanite, and apatite. This montage puts Figure 4.62 into context and shows the protomylonitic texture well. Deformed muscovite porphyroblasts, with the largest measuring ~4300ppm on its long axis. These porphyroblasts have undergone intense strain; evidenced by the fracturing, the mica 'fish' texture of the grains on the right, the deformed cleavages, highlighted by quartz precipitating within cleavage fractures. A fractured plagioclase grain lies within the intersection of the three large muscovite porphyroblasts. Within this plagioclase fracture, quartz has precipitated. Quartz is the common phase to precipitate within fractures; it can also be seen within muscovite grains. This montaged image communicates the anastomosing nature of the sheared mica aggregates, and the varying domains; note how some matrix regions are heavily quartz-dominated, but others attain higher proportions of muscovite and plagioclase.

S1(B) MP13 (Area 3)

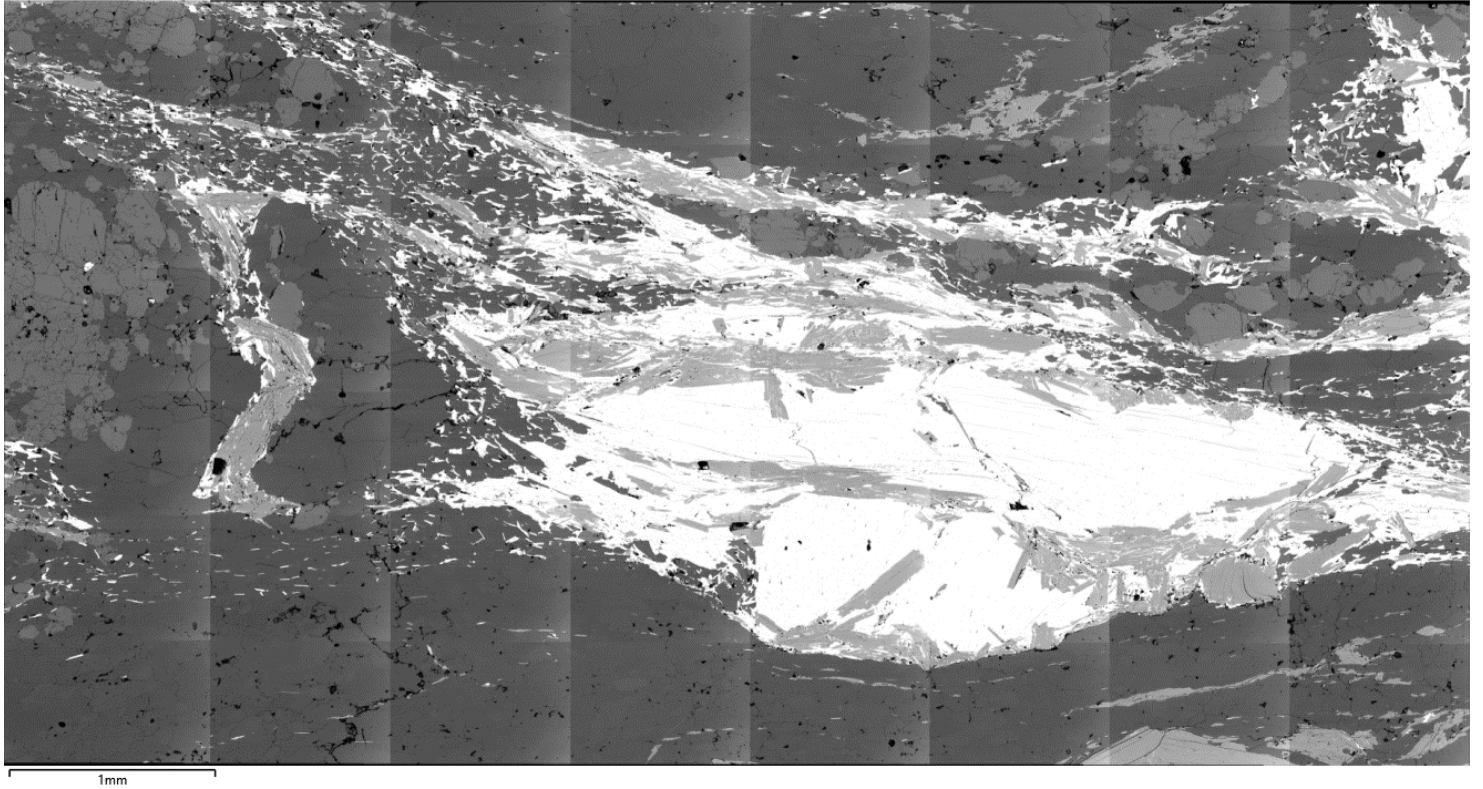


Figure 4.65: 1(B)MP – Montaged back-scattered Electron Image (No.13; Area 3); Black = Holes. Dark grey = quartz, medium-dark grey = albite, light grey = muscovite, grey-white = epidote, white = biotite (minor titanite/epidote). This image shows an aggregation of biotite grains. The occurrence of biotite as porphyroblasts is rare, and this is the only example within 1(B)MP. The decussate textures observed for micas is well evidenced in this image, as well as the variance of micas oriented parallel to the fabric and some that appear more random. In this section, quartz dominates the matrix.

S1(B) MP.14 (Area 4)

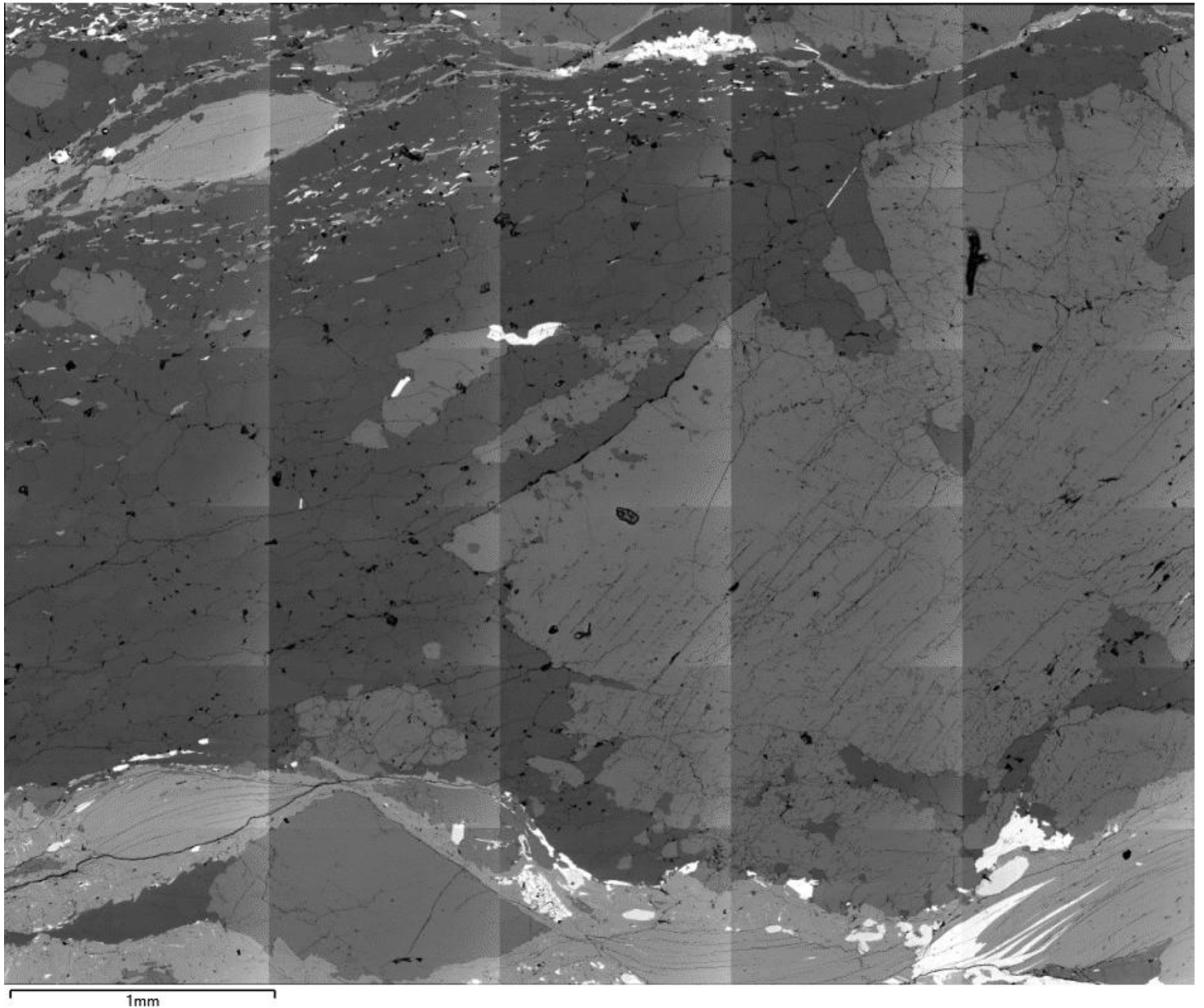


Figure 4.66: 1(B)MP – Montaged Back-scattered Electron Image (No.14; Area 4); Black = Holes. Dark grey = quartz, medium-dark grey = albite, light grey = muscovite, grey-white = epidote, white = biotite, titanite and chlorite. This montaged electron image displays a large plagioclase porphyroblast, with clear bookshelf fracturing. Quartz has precipitated within the fractures. Toward the rims of the plagioclase porphyroblast, one can see inclusions of quartz, often occurring as 'strings of beads'. Quartz dominates the matrix, however regional domains can be seen, with much more muscovite and plagioclase toward the top.

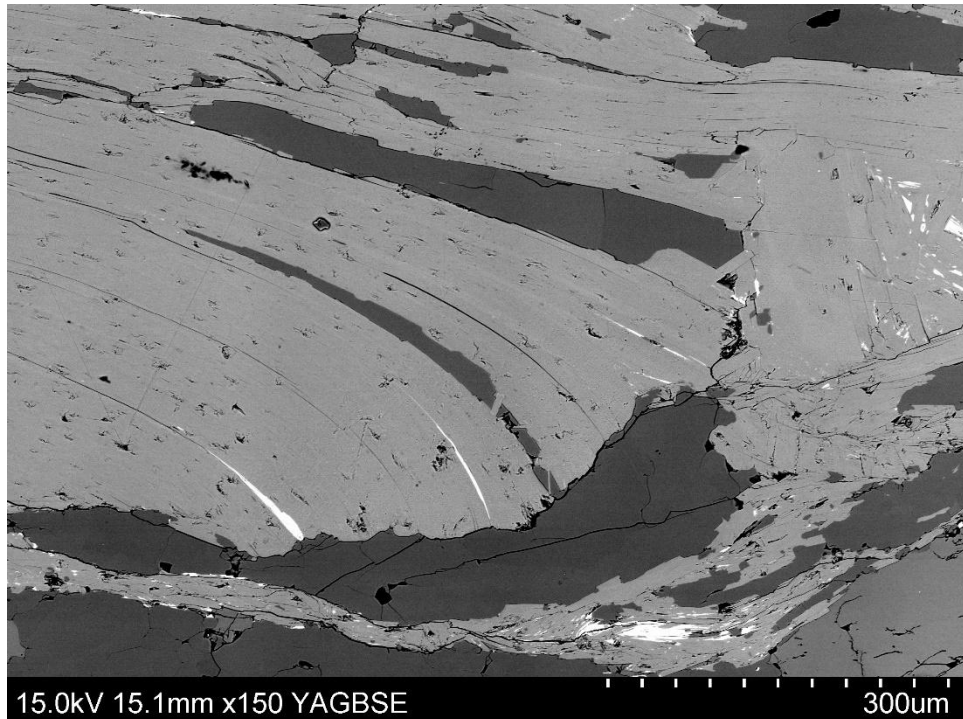


Figure 4.67: Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.025). This image evidences the deformation observed within micas. Deformed cleavages within the muscovite grains have facilitated precipitation of quartz and biotite within fractures. At the bottom a micaceous aggregate meanders across the image, where it joins a more decussate muscovite aggregate. This texture is likely due to slippage along cleavage planes during shear strain.

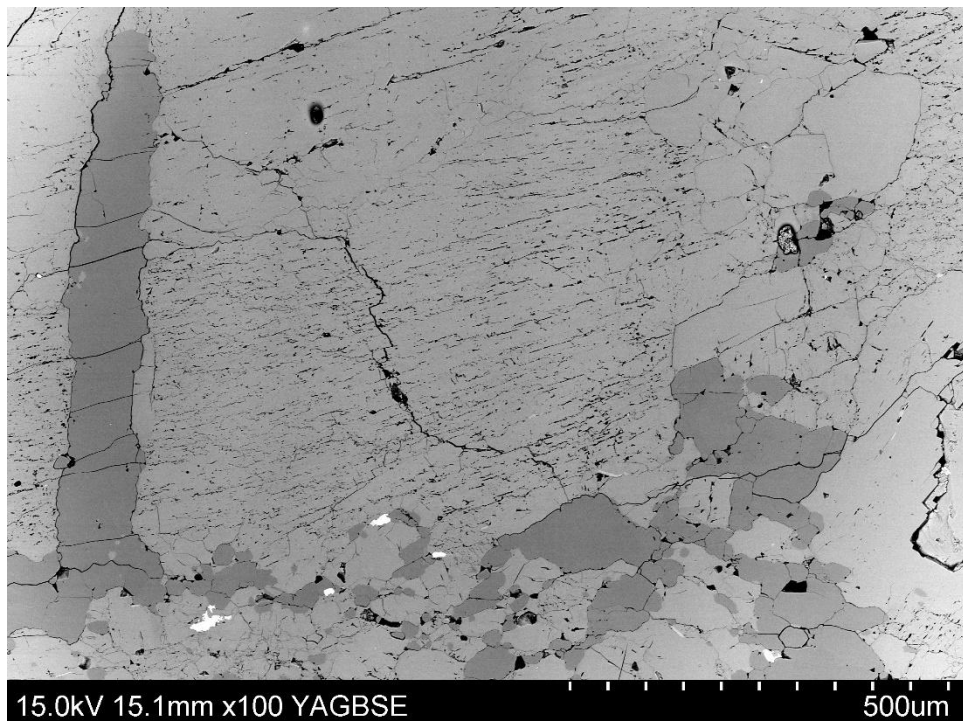


Figure 4.68: Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.027). Quartz infill along a fractured plagioclase porphyroblast. Toward the bottom quartz grains occur as beads. This may be due to heightened strain enhancing nucleation rate, facilitating numerous quartz grains to precipitate along these fractures. To the right, the plagioclase does not appear altered/speckled to the same extent as within most of the porphyroblast. This may be due to recrystallisation.

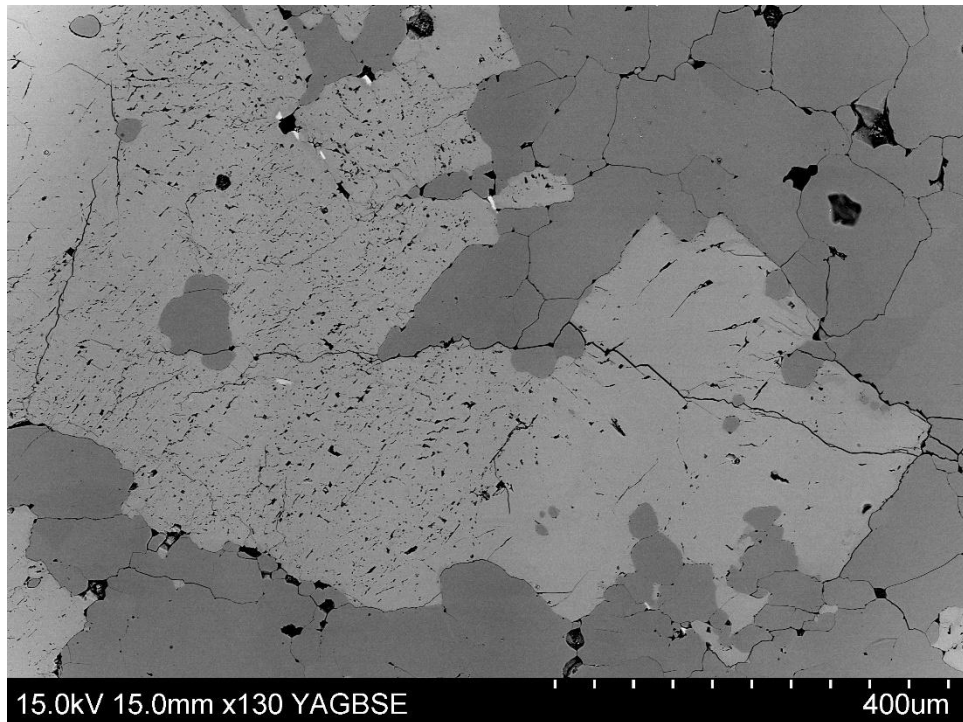


Figure 4.69: Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.031). Plagioclase (light grey) and quartz (dark grey) show interesting boundary relationships. The speckled appearance of plagioclase in thin section is accounted for by the inclusions observed here. Plagioclase on the right is not as intensely speckled as the rest. Quartz 'beads' intrude into the plagioclase, indicating simultaneous growth. The occurrence of quartz as rounded beads is due to the break-up of these grains into lower energy forms (Holness & Clemens, 1999). Within the quartz one can see fractures which evidence subgrain formation due to shearing.

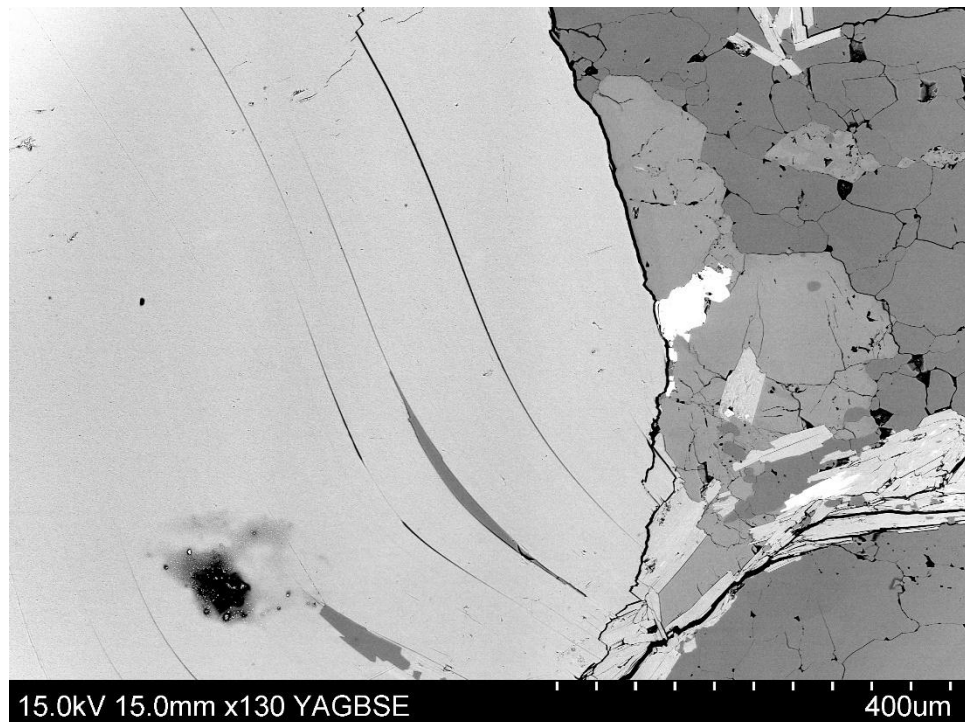


Figure 4.70: Back-scattered Electron Image of Mataketake Pegmatite (1(B)MP.035). A deformed muscovite porphyroblast containing quartz inclusions along deformed cleavage fractures. To the right, an opaque phase, likely titanite/ilmenite, contrasts to the surrounding feldspar/muscovite. Quartz shows subgrain formation again, visible through fractures. A micaceous aggregate occurs to the bottom right, which appears to be sourced from the mica porphyroblast.

1.AS.MP.B.001

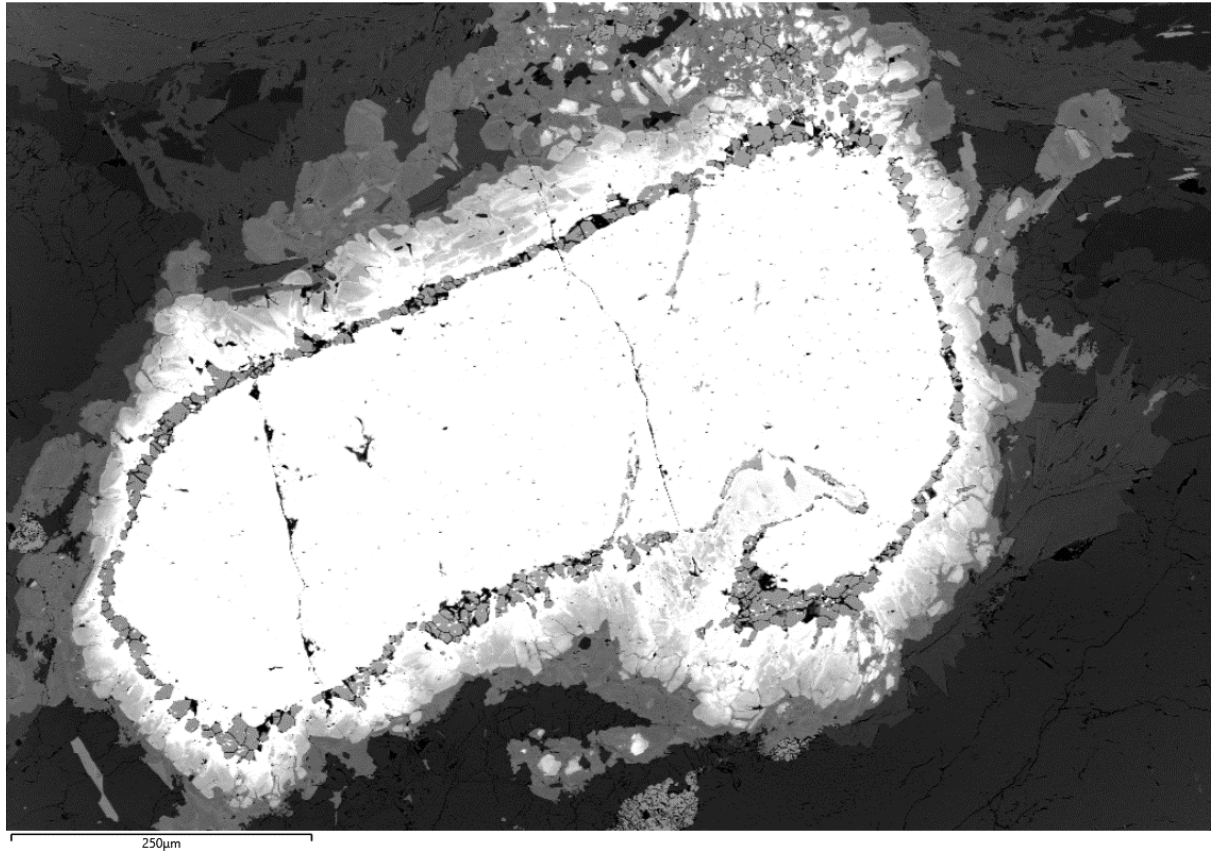


Figure 4.71: Back-scattered Electron Image of Mataketake Pegmatite (1.AS.MP.B 001). A coarse monazite grain within the pegmatite. Surrounding the monazite is a fluorapatite and epidote rim. Epidote is more Ca-enriched when more distal from the monazite. Conversely, epidote is more Ce, La and Nd rich adjacent to the monazite grain, and may be identified as allanite. The monazite is fractured, with epidote precipitating within this fracture. Plagioclase (roughly oligoclase) dominates the rest of the image along with muscovite, although these are difficult to make out.

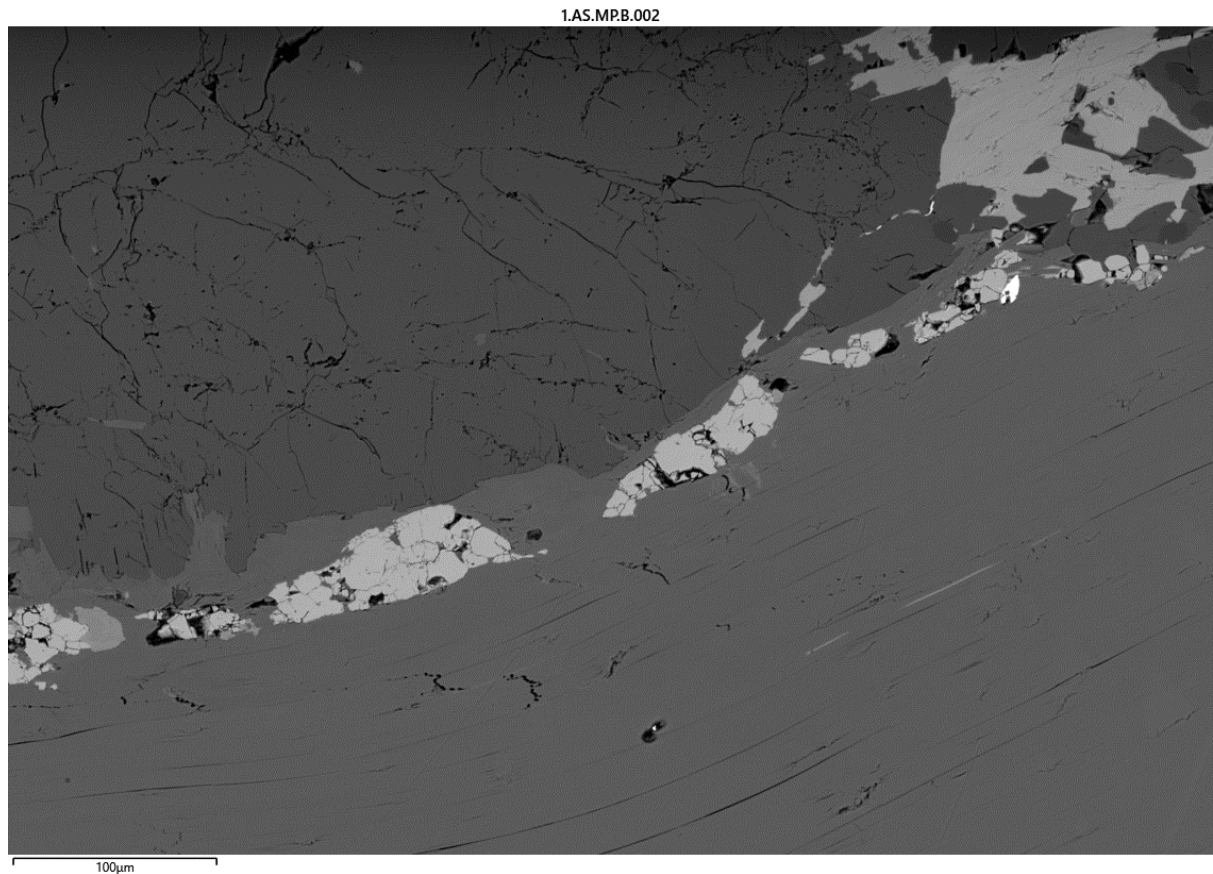


Figure 4.72: Back-scattered Electron Image of Mataketake Pegmatite (1.AS.MP.B 002). Plagioclase (top left), contrasts to a muscovite porphyroblast (bottom right). Along the rim of the muscovite porphyroblast, epidote has precipitated, along with some apatite. To the top right, an aggregation of biotite grains appears, which are generally aligned with the muscovite grain. Note the deformation within the muscovite; the cleavage planes are bent, and fractures appear.

4.4 Summarising Key Textures and Interpretations

Petrographic analyses show a suite of metamorphic rocks, with increasing intensity of metamorphic deformation closer to the Alpine Fault. They range from greenschist-facies chlorite schists through to lower-amphibolite facies schists. Within this progression, common mineralogical and textural changes are observed. Notably, chlorite decreases in abundance, whilst biotite increases in abundance. Grain size also increases significantly with greater metamorphic intensity. Deformation textures were visible, particularly in schists more proximal to the Alpine Fault. Micas appear sheared, and form anastomosing streaks which highlight schistose foliation. Within these streaks, mica grains are often aligned, but occasionally form decussate textures. ‘Mica-fish’ are also observed, with other minerals (commonly quartz) precipitating along deformed cleavage fractures. Quartz displays subgrain deformation and albites show deformation twins. These textures indicate a second period of deformation.

Unlike previous descriptions of these metamorphic rocks (e.g., (Briggs & Cottle, 2018; Wallace, 1974)), we observe no K-feldspar. Similarly, the Mataketake Pegmatites also show no K-feldspar.

SEM-EDS analyses corroborated this absence of K-feldspar. Dyck et al. (2020) communicate how granitic melts in orogenic hinterlands are initially produced via muscovite dehydration melting. In fluid-absent scenarios, the dominant reaction is muscovite + quartz = K-feldspar + sillimanite + monzogranitic melts. In this situation, K-feldspar precipitates as a peritectic phase (Dyck et al. (2020)). Conversely, in settings where water-vapour is present in excess, muscovite primarily breaks-down to produce sillimanite + melt (Dyck et al., 2020). Any produced K-feldspar can only be generated due to melt crystallisation in fluid-present muscovite dehydration (Dyck et al. (2020)). Wallace (1974) observed myrmekitic intergrowths between K-feldspar and quartz within the pegmatite. As such, we searched for myrmekitic intergrowths, as these may be indicative of where K-feldspar was once present. No myrmekitic intergrowths were noted in the pegmatite. As such, the lack of K-feldspar in pegmatites of this study is interpreted to be indicative of fluid-present melting, based on the findings of Dyck et al. (2020). This interpretation will be investigated and validated through later chapters of this thesis.

The Mataketake Pegmatite is texturally different to its adjacent Alpine Schist (Figure 4.25). Grain size is drastically coarser, and larger porphyroblasts of muscovite and feldspar attain sizes up to ~3mm in length. Feldspar porphyroblasts display bookshelf fracturing, kink-banding and deformation twins. Fractures are infilled with quartz. While these textures have some features in common with pseudomorphed melt in grain boundary films observed by (Rushmer, 1996), observations clearly pointed to quartz infill via solution-precipitation creep (fluid assisted mass transfer). Other deformation textures are also abundant, in the form of mica-fish, shearing of mica grains producing anastomosing micaceous streaks, and subgrain deformation in quartz. Mineralogically, the Mataketake Pegmatite and Alpine Schist differ in relative abundances of the four dominant phases (quartz, albite, muscovite and biotite). The plagioclase component in the pegmatite appears notably increased relative to the schist, whereas the micaceous components appear to be sparser in the pegmatite. As both the Mataketake Pegmatite and Alpine Schist are dominated by the same four phases, their relative quantities may be indicative of melting processes. This is something we aim to confirm through quantification in subsequent sections. Additionally, garnet is absent in the Mataketake Pegmatite, and the quantity of minor phases varies.

We do not observe an increase in the fraction of mafic content at the schist-pegmatite border, which would have been indicative of in-situ partial melting of the schist during metamorphism (Wallace, 1974). Therefore, we interpret that melting/extraction of schist immediately adjacent to the pegmatite has not been significant. Instead, we propose that the pegmatite has been injected via a localised flow. Holistically, the intersection of low-degree melting, intrusion and subsequent strain have been the dominant controls on the petrography, and therefore may have important implications for geochemistry.

5 MINERAL GEOCHEMISTRY

5.1 Mineralogical Abundances

Chemical mapping in Aztec and subsequent ImageJ analysis of 1.AS and 1(B)MP, detailed in Section 3.3, enabled a calculated estimate of whole-rock mineralogical compositions (Table 5.1). As well as major phases, these calculations record the existence and variation of minor phases, providing important insight into trace element geochemistry. It is difficult to quantify uncertainty within these estimates, however garnet is likely underrepresented. Due to its common mode of occurrence as discrete porphyroblasts, it is rarely included in chemical maps.

Table 5.1: Mineralogical Composition of Alpine Schist (1.AS) and Mataketake Pegmatite (1(B)MP). Calculated from pixel content of chemical maps, and further refined using ImageJ.

Phase	% 1.AS	% 1(B)MP	Calculated mineralogical abundances align with petrological observations recorded in Section 4. The dominance of the four major phases, quartz, plagioclase, muscovite, and biotite is reflected in Table 5.1; they constitute ~98% of 1.AS and >99% of 1(B)MP. Quartz content remains consistent, with an increase of just over 1%. Plagioclase content increases significantly, with a 50% increase from 1.AS, reaching 33.5% in the pegmatite. Muscovite and biotite decrease notably, from 24.2% to 19.4%, and 13.5% to 7.6% respectively.
Quartz	37.98	39.15	
Plagioclase	22.52	33.50	
Muscovite	24.15	19.41	
Biotite	13.50	7.58	
Epidote	0.75	0.16	
Fluorapatite	0.17	0.042	
Titanite	0.45	0.014	
Fe-Sulphides/Oxides	0.19	0	
Chlorite	0.032	0.14	
Apatite	0.0039	0.00059	
Zircon	0.010	0.0011	
Garnet	0.25	0	
Ilmenite	0.015	0.0017	
Zeolite	0	0.00029	
Monazite	0	0.0064	
Opaques	0	0.00047	
Total:	100	100	

5.1.2 Minor Phases

EDS analyses allowed for better identification of minor phases. Minor phases refers to phases that do not make up a significant portion of the mineral assemblage, anything apart from micas, feldspar and quartz in this case study. Most accessory phases decrease in abundance from the schist to the pegmatite: epidote, fluorapatite, titanite, Fe-oxide, apatite, zircon, garnet, ilmenite. Conversely, chlorite increases. Other phases, like zeolite, and monazite are present in 1(B)MP but have not been recorded in 1.AS. EDS analyses on minor phases are shown in Tables 5.2-5.12.

*Table 5.2: Garnet Average Compositions
1.AS (n=10)*

Element	Oxide %	σ	StDev
Si	40.92	0.18	1.99
Al	23.10	0.13	0.20
Fe	23.96	0.18	3.84
Ca	8.20	0.08	1.05
Mn	1.09	0.10	1.34
Na	0.31	0.08	0.93
Mg	2.24	0.06	0.27
K	0.18	0.06	0.53

Table 5.3: Epidote Average Compositions

1.AS (n=11)				1(B)MP (n=12)		
Element	Oxide %	σ	StDev	Oxide %	σ	StDev
Si	41.54	0.32	1.29	42.38	0.24	1.15
Al	29.86	0.25	1.42	29.83	0.19	1.39
Ca	20.13	0.20	2.43	19.34	0.15	2.57
Fe	5.87	0.23	1.22	5.70	0.17	0.85
Na	0.15	0.07	0.39	-	-	-
Mn	0.12	0.10	0.39	0.01	0.04	0.04
Ce	1.12	0.18	1.63	1.70	0.21	2.54
Mg	0.06	0.06	0.18	-	-	-
K	0.05	0.05	0.16	0.16	0.06	0.52
Nd	0.54	0.19	0.88	0.35	0.26	0.79
La	0.46	0.17	0.76	0.54	0.26	1.21
Y	0.11	0.15	0.33	-	-	-

Table 5.4: (Fluor)Apatite Average Compositions

1.AS (n=10)				1(B)MP (n=5)		
Element	Oxide %	σ	StDev	Oxide %	σ	StDev
Ca	51.87	0.21	0.32	50.69	0.18	0.34
P	43.86	0.24	0.24	43.86	0.22	0.43
F	0.00	0.21	0.00	0.00	0.18	0.00
Fe	0.10	0.08	0.21	-	-	-
Al	0.19	0.08	0.42	0.48	0.02	0.68
Si	0.08	0.11	0.25	0.22	0.01	0.02

Table 5.5: Apatite Average Compositions

1.AS (n=1)				1(B)MP (n=2)		
Element	Oxide %	σ	StDev	Oxide %	σ	StDev
Ca	55.34	1.39	0.00	59.95	1.64	14.68
P	44.66	1.76	0.00	24.69	1.72	10.61
Si	-	-	-	8.65	1.12	0.84
Al	-	-	-	2.66	1.02	2.66
Mg	-	-	-	4.05	0.95	0.58

Table 5.6: Titanite Average Compositions

1.AS (n=6)				1(B)MP (n=5)		
Element	Oxide %	σ	StDev	Oxide %	σ	StDev
Si	34.47	0.43	1.56	35.15	0.46	0.44
Ti	34.03	0.50	2.62	34.88	0.54	0.47
Ca	26.60	0.35	1.89	27.24	0.36	0.29
Al	3.67	0.21	1.80	2.59	0.21	0.30
Fe	0.73	0.16	0.61	0.13	0.15	0.27
Na	0.22	0.14	0.48	-	-	-
K	0.22	0.08	0.33	-	-	-
Mg	0.08	0.08	0.18	-	-	-

*Table 5.7: Accessory Phases: Fe-Sulphides/Oxides Average Compositions
1.AS (n=4)*

Element	Oxide %	σ	StDev
Fe	62.54	0.98	13.95
Si	11.49	0.67	6.45
Al	7.55	0.54	4.33
P	3.23	0.72	2.51
S	14.83	0.23	25.68
Ni	0.37	0.12	0.64

Table 5.8: Average Chlorite Compositions

1.AS (n=1)				1(B)MP (n=2)		
Element	Oxide %	σ	StDev	Oxide %	σ	StDev
Si	31.24	0.84	0.00	32.02	0.42	0.67
Fe	31.19	0.94	0.00	26.83	0.46	0.5
Al	23.91	0.73	0.00	26.72	0.36	0.76
Mg	12.35	0.55	0.00	14.19	0.27	0.15
K	1.30	0.25	0.00	0.03	0.01	0.03
Na	0.00	0.37	0.00	-	-	-
Mn	-	-	-	0.22	0.03	0.22

Table 5.9: Zircon Average Compositions

1.AS (n=5)				1(B)MP (n=2)		
Element	Oxide %	σ	Stdev	Oxide %	σ	Stdev
Zr	61.65	2.99	10.56	64.42	1.49	2.49
Si	36.63	2.5	7.56	35.59	1.21	2.49
Al	1.72	0.25	3.07	-	-	-

Table 5.10: Average Ilmenite Composition

1.AS (n=3)				1(B)MP (n=1)		
Element	Oxide %	σ	St.Dev	Oxide %	σ	St.Dev
Ti	55.17	0.54	0.54	55.19	0.82	0.00
Fe	41.36	0.51	0.54	40.89	0.78	0.00
Mn	3.19	0.28	0.21	3.92	0.44	0.00
Si	0.27	0.07	0.20	-	-	-

*Table 5.11: Average Zeolite Composition**1(B)MP (n=1)*

Element	Oxide %	σ
Si	57.17	1.62
Al	23.28	1.05
Ca	15.74	0.88
Fe	3.81	0.93

*Table 5.12: Average Monazite Composition**1(B)MP (n=1)*

Element	Oxide %	σ	St.Dev
P	32.42	0.5	0.00
Ce	27.99	0.58	0.00
La	13.83	0.49	0.00
Nd	10.64	0.56	0.00
Th	8.21	0.37	0.00
Pr	2.79	0.57	0.00
Sm	1.71	0.52	0.00
Si	1.31	0.16	0.00
Ca	1.10	0.11	0.00

5.2 Major Element

5.2.1 Plagioclase

Analysed feldspars in both 1.AS and 1(B)MP were solely plagioclase feldspars. No other feldspars were observed. Despite other studies (Beyssac et al., 2016; Briggs & Cottle, 2018; Wallace, 1974) all observing K-feldspar (Or_{92-95} for Wallace (1974)), there is no K-feldspar in the analysed samples of this case study. Significant time was spent scouring samples for K-feldspar, as its significance in melting reactions, and its precipitation as a peritectic phase can inform on processes (Briggs & Cottle, 2018; Dyck et al., 2020; Icenhower & London, 1995; Inger & Harris, 1993; Weinberg & Hasalová, 2015). However, other literature reports a lack of K-feldspar within amphibolite-facies schists (Murphy, 2010), and lithological heterogeneity is well documented throughout the metamorphic rocks of the South Island, New Zealand.

Major element geochemistry of plagioclase differed between the three analysed samples (1.AS, 1.AS.H and 1(B)MP). Plagioclase within the pegmatite is compositionally distinct from both 1.AS and 1.AS.H, indicating they are newly formed. Despite being of similar metamorphic facies, the variation in plagioclase composition within the Alpine Schists communicates source rock heterogeneity within the greywackes/pelitic greywackes of the Torlesse Terrane, and a varying metamorphic regime along the Alpine Fault (Beyssac et al., 2016).

Anorthite Content (mol%)	1.AS	SStDev	n	1(B)MP	StDev	n	1.AS.H	StDev	n
Sample Mean	28.1	6.45	36	18.1	1.29	44	22.6	2.52	35
Sample Max An	38.8	Na	36	21.3	Na	44	28	Na	35
Sample Min An	18.4	Na	36	15.5	Na	44	18.6	Na	35
Sample Mean C	31.9	4.90	13	18.5	1.56	17	22.5	3.15	10
Sample Mean R	25.9	5.59	11	17.8	0.96	17	22.4	2.00	11
Sample Mean (M)	23.0	5.00	8	17.8	1.04	10	22.8	2.45	13

Table 5.13: Mean anorthite content of plagioclase feldspars in Alpine Schist (1.AS), Mataketake Pegmatite (1(B)MP, and Alpine Schist from Hare Mare Creek (1.AS.H). C = core of grains. R = grain rims. (M) = matrix grains. See Chapter 3 for details on intragrain locations.

EDS analyses show that K_2O averages 0.065wt% 1.AS (± 0.028 wt%), and 0.028wt% in 1(B)MP (± 0.068 wt%). No K was identified in EDS for 1.AS.H. Figure 5.1 shows the composition of analysed plagioclases across the three rock-types.

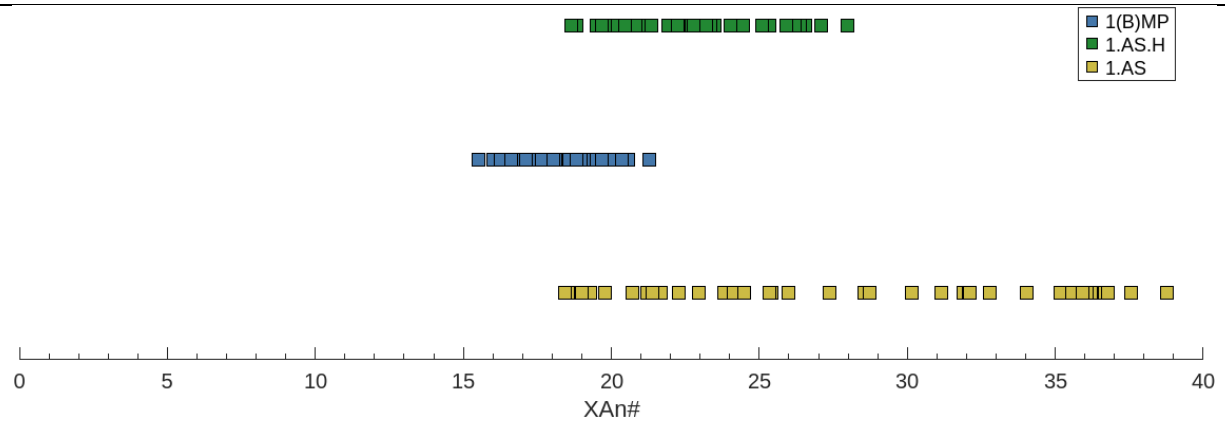


Figure 5.1: Anorthite content of plagioclase compositions within analysed rock samples.

In particular, 1.AS shows a much wider range from An18.4 to An38.8, compared to the much more confined compositions of 1(B)MP, from An15.5 to An21.3 (Figure 5.1). 1(B)MP therefore occupies a lesser range of plagioclase compositions, and reaches lower An values. There was no observed variance within this study for cores, rims, and matrix plagioclase grains (Table 5.13). Rims were observed petrographically. However, due to their size, we were unable to analyse their geochemistry. Murphy (2010) identifies oligoclase rims on albite grains, much like in this study (see Section 4 & Figure 5.2).

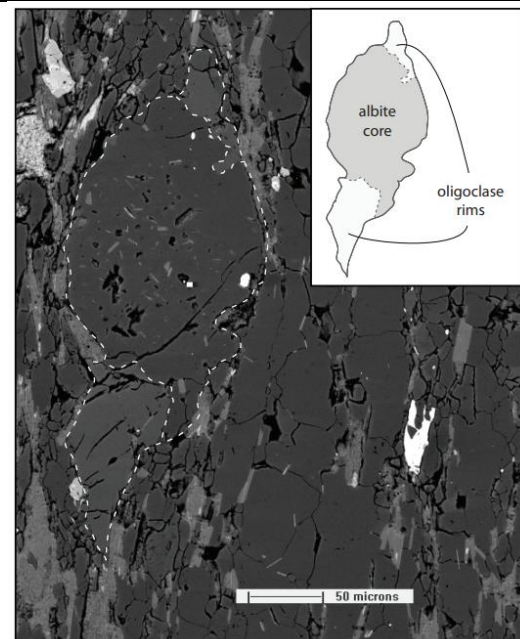


Figure 5.2: Albite grain rimmed by oligoclase, from Newton Range (Murphy, 2010).

5.2.2 Muscovite

‘Pure’ muscovite can be attributed the following formula: $KAl_2(Si_3Al)O_{16}(OH_2)$. However, numerous complex cation exchanges can occur, and therefore the formula can be considered as follows (Li et al., 2021):

$XY_{\sim 2}\blacksquare_{1-0}Z_4O_{10}(W_2)$ where:

▪ represents a vacancy

$X = K^+, Na^+, \text{ but also } Rb, Cs, Ba, \text{ \& } NH_4 \text{ \& } Ca$

$Y = Al^{3+}, Fe^{3+}, Fe^{2+}, Mg^{2+}, \text{ but also } Li, Mn^{2+}, Cr, V \text{ and others}$

$Z = Si^{4+}, Al^{3+}, B, Be, \text{ and } Fe^{3+}$

$W = OH, F, Cl, \text{ and } S$

Muscovite comprises 24.15% of 1.AS, and 19.41% of 1(B)MP (Table 5.1). There is little/no muscovite observed in 1.AS.H, reflecting composition heterogeneity within the Alpine Schist, derived from variations in the Torlesse Terrane and the varying P-T conditions across the metamorphic belt (Beyssac et al., 2016). Stoichiometry was calculated on a 24 (O, OH, F) basis, or 22 O. There is no chemical evidence for zonation within analysed muscovites and there is no notable deviation between cores, rims, and matrix grains. Mica compositions were plotted on the mgli ($Mg - Li$ (a.p.f.u)) vs feal ($^{VI}Fe_{tot} + Mn + Ti - ^{VI}Al$ (a.p.f.u)) diagram After Tischendorf et al. (2007); Tischendorf et al. (2004). All are contained within the ‘muscovite’ section of this plot (Figure 5.3). 1.AS is more phengitic, whereas 1(B)MP attains higher Al^{VI} values (lower feal) meaning that elemental substitution into the octahedral site must be limited (Tischendorf et al., 2007), and is more homogenous (Figure 5.3). Table 5.14 states the average compositions of muscovites in 1.AS and 1(B)MP. The Otago Schist has more phengitic compositions than the Alpine Schist (Little et al., 1999). Figure 5.4 displays the analysed muscovite compositions in relation to data from Murphy (2010) and Little et al. (1999). 1.AS groups toward the muscovite compositions of the Alpine Schist, with some muscovite samples bridging between Alpine Schist and Otago Schist fields of Little et al. (1999).

Muscovite samples were separated into core, rim and matrix locations. There is no recorded trend concerning intragrain location and elemental abundances.

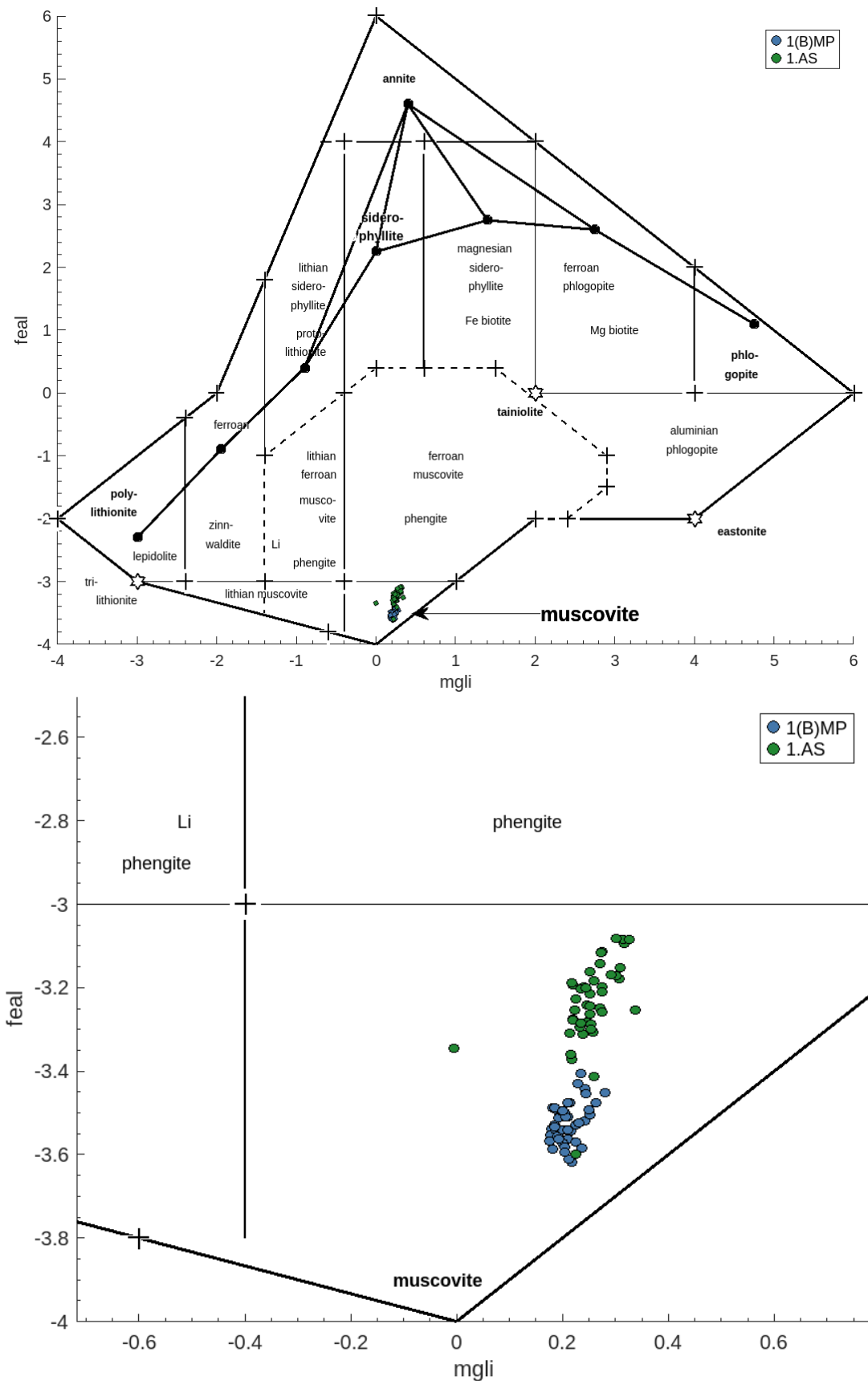


Figure 5.3: **Top:** Muscovite compositions plotted on mgli v feal, after Tischendorf et al. (2007); Tischendorf et al. (2004). **Bottom:** Close-up of muscovite compositions in the pegmatite (1(B)MP) and Alpine Schist (1.AS).

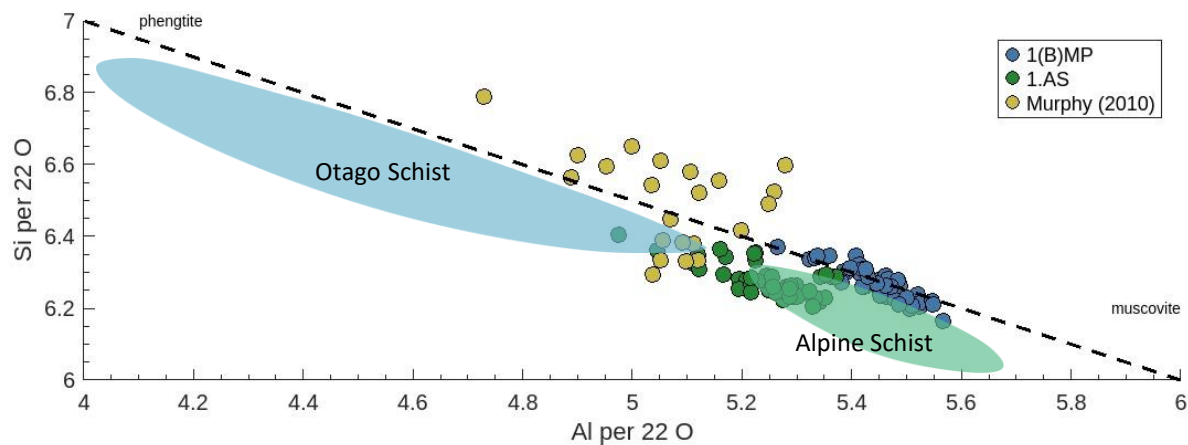


Figure 5.4: Muscovite compositions (1.AS, 1(B)MP and those from nearby Newton Range (Murphy (2010)) relative to identified compositions of Otago Schist and Alpine Schist muscovites (Little et al., 1999).

5.2.3 Biotite

Biotite is the name given to a group of minerals, namely phlogopite, siderophyllite and eastonite.

Biotite group minerals attain the general formula:



My study looks at biotite phases in Alpine Schist from Hare Mare (1.AS.H), Alpine Schist from the Mataketake Region (1.AS) and the Mataketake Pegmatite (1(B)MP). Biotite comprises 13.5% by are of the 1.AS and only 7.6% 1(B)MP; a reduction of ~50%. The compositions of biotites are displayed in Table 5.14.

1.AS.H biotites cluster toward the phlogopite region of the Tischendorf plot, illustrating their depletion in Fe, and enrichment in Mg (Figure 5.6 ((Tischendorf et al., 2007))). Both 1.AS and 1(B)MP are situated more toward siderophyllite compositions. Consequently, the principal compositional difference between biotites at Hare-Mare, and biotites in the Mataketake region (1.AS & 1(B)MP) is the Mg:Fe abundance. Notably, biotite from 1(B)MP appears as 2 discrete clusters in Fe and Al abundances (Figures 5.5, 5.6 & 5.7). Major elements were obtained from SEM-EDS, where detection limits can result in analytical uncertainty. These two clusters average compositions reasonably close to 1.AS, which seems to bridge the gap between these clusters (Figures 5.5, 5.6 & 5.7). Due to the uncertainty within major elements, it is difficult to make any compositional comparisons between 1.AS and 1(B)MP. There is no significant trend for cores, rims, and matrix grains for biotite.

Table 5.14: Average mica compositions in 1(B)MP, 1.AS and 1.AS.H (wt% oxide). “ σ ” = standard deviation.

	Biotite (1(B)MP)		Biotite (1.AS)		Biotite (1.AS.H)		Muscovite (1(B)MP)		Muscovite (1.AS)	
	n = 33	σ	n = 32	σ	n = 41	σ	n = 45	σ	n = 44	σ
SiO ₂	38.66	1.74	38.38	0.63	40.70	0.20	49.92	0.40	49.48	0.45
TiO ₂	2.30	0.25	1.34	1.01	1.94	0.45	0.17	0.06	0.16	0.17
Al ₂ O ₃	19.52	0.89	19.19	0.55	20.07	0.44	36.76	0.45	35.04	0.54
FeO	21.79	2.66	22.20	1.19	16.26	0.29	1.64	0.18	2.23	0.47
MnO	0.22	0.02	0.24	0.03	0.04	0.01	0.01	0.00	0.02	0.00
MgO	8.12	0.53	8.99	0.30	12.19	0.25	1.15	0.13	1.36	0.27
CaO	0.01	0.02	0.03	0.05	0.02	0.04	-	-	-	-
Li ₂ O	0.04	0.00	0.04	0.00	0.05	0.00	0.01	0.00	0.01	0.00
Na ₂ O	0.07	0.02	0.09	0.05	0.10	0.03	0.26	0.29	0.31	0.19
K ₂ O	9.61	0.38	9.83	0.42	8.84	0.14	10.17	0.14	11.39	0.33
BaO	0.13	0.02	0.11	0.02	0.10	0.01	0.35	0.08	0.29	0.06
Total	100.46		100.44		100.31		100.45		100.29	

No. of ions on the basis of 22 (O, OH, F) (assuming ideal occupancy of OH site (OH = 2)).

Si	5.587	8.00	5.539	8.0	5.670	8.00	6.272	8.00	6.279	8.00
Al ^{IV}	2.413		2.461	0	2.330		1.728		1.721	
Al ^{VI}	0.911		0.803		0.965		3.714		3.521	
Ti	0.237	5.59	0.196		0.205	5.63	0.016	4.12	0.047	4.07
Fe	2.644		2.680	5.6	1.895		0.172		0.237	
Mn	0.027		0.029	6	0.004		0.002		0.002	
Mg	1.748		1.933		2.532		0.215		0.258	
Li	0.022	1.820	0.021		0.029	1.64	0.004	1.89	0.005	2.11
Ca	0.002		0.004		0.003		-		-	
Na	0.038		0.052	1.8	0.056		0.069		0.084	
K	1.775		1.810	7	1.571		1.797		2.012	
Ba	0.007		0.006		0.005		0.019		0.016	

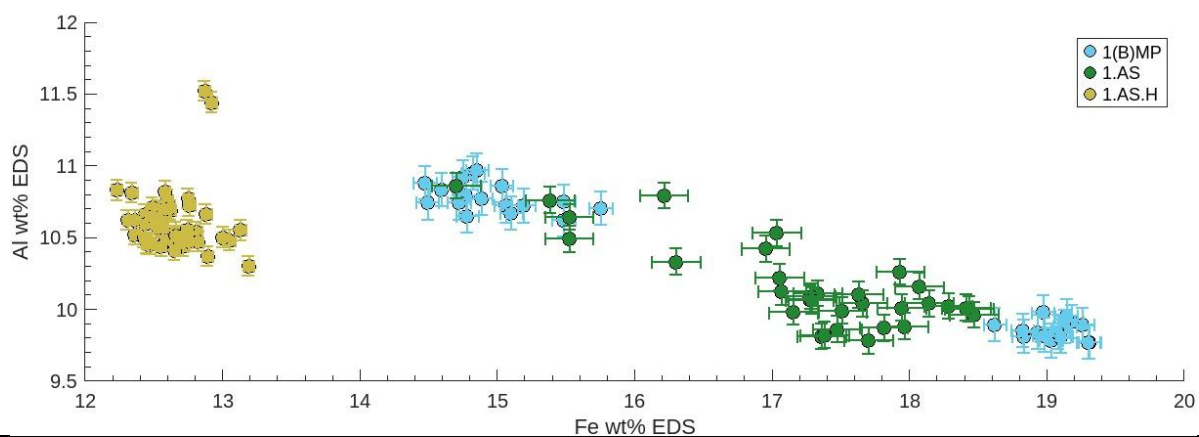


Figure 5.5: Fe v Al (wt%) EDS data, showing two compositional clusters for Fe and Al within 1(B)MP.

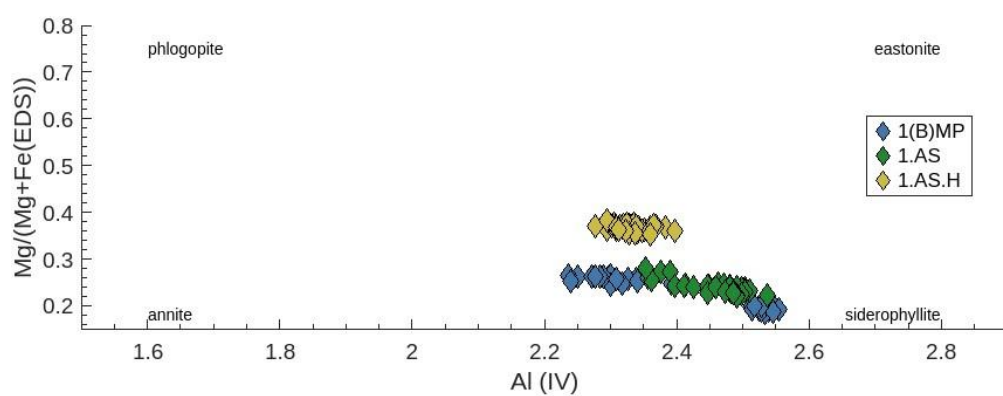


Figure 5.6: Biotite compositions on Al (IV) vs Mg/(Mg+Fe) plot. A: EDS data. B: Laser-ICP data.

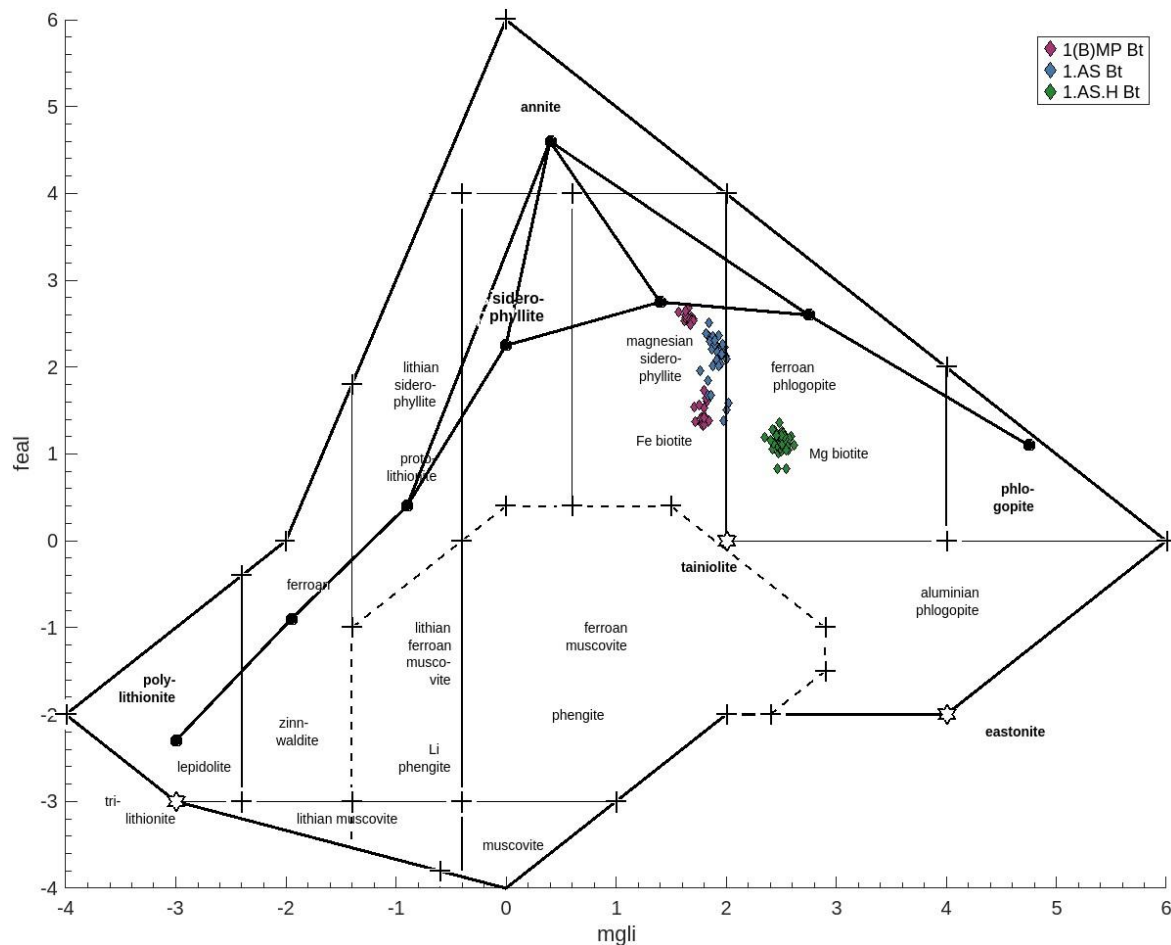


Figure 5.7: Biotite compositions after (Tischendorf et al., 2007; Tischendorf et al., 2004).

5.3 Trace Elements

5.3.1 Plagioclase

Li is not preferentially hosted in plagioclase, with 31/36 samples in 1.AS below detection limits, and a 42/44 samples in 1(B)MP below detection limits. Sr, Pb and Ba are perhaps the most significant of the analysed trace elements; all 3 show distinct compositional data for plagioclases within the 3 rock samples (Figure 5.8 & Table 5.15). Strontium shows significant variation between the 3 samples and is depleted in 1(B)MP compared to the schists. Pb shows the same trend. Ba is slightly different; 1(B)MP and 1.AS.H form two clusters, whereas 1.AS is much more spread in its Ba contents. Other LILE (Eu, K, Rb, Cs) are depleted in the feldspars. Eu averages 0.70ppm in 1(B)MP ($n=40$, $\sigma=0.35$ ppm), 0.61ppm in 1.AS ($n=28$, $\sigma=0.516$ ppm) and 0.04ppm in 1.AS.H ($n=21$, $\sigma=0.03$). Rb and Cs are mostly below LOD; with 1.AS averaging LOD of 1.12ppm (Rb) and 0.25ppm (Cs), and 1(B)MP averaging LOD of 0.47ppm (Rb) and 0.30ppm (Cs). HFSE (Ti, Y, Eu, La) are also depleted in the feldspars, with most data below LOD. La has enough data above LOD to comment on, it averages 1.01ppm in 1(B)MP ($n=37$, $\sigma=0.87$ ppm), 0.27ppm in 1.AS ($n=25$, $\sigma=0.57$ ppm) and 0.001ppm in 1.AS.H ($n=15$, $\sigma=0.03$ ppm). This may show a relative enrichment in the pegmatite, but high standard deviation limits the significance of mean averages. Other LREE (La, Ce, Pr) are of low

concentrations and relatively high =standard deviations but appear to show a similar trend of relative enrichment in the pegmatite. Ce averages 1.30ppm in 1(B)MP (n=39, σ =1.29ppm), 0.41ppm in 1.AS (n=30, σ =0.89ppm) and 0.004ppm in 1. AS.H (n=17, σ =0.008ppm). Whilst Pr averages 0.17ppm in 1(B)MP (n=25, σ =0.10ppm), 0.05ppm in 1.AS (n=17, σ =0.096ppm), and 0.0002ppm in 1.AS.H (n=17, σ =0.0004ppm). Many feldspar samples for 1.AS.H were below LOD for LREE, with less below LOD for 1.AS and 1(B)MP.

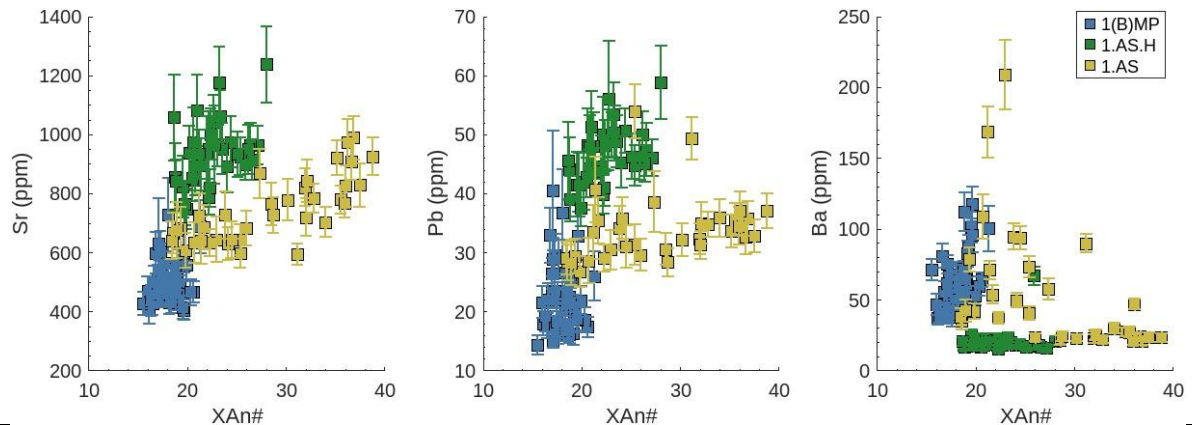


Figure 5.8: A: Xan v Sr (ppm). B: Xan v Pb (ppm). C: Xan v Ba (ppm). These three scatter plots illustrate the 3 different compositions of the plagioclases within samples. Average LOD were as follows: 1.AS.H: Sr=89.73ppm, Pb=0.35ppm, Ba=3.08ppm, 1(B)MP: Sr=54.22ppm, Pb=0.47ppm, Ba=7.53ppm, 1.AS: Sr=64.91ppm Pb=3.26ppm, Ba=5.91ppm

Table 5.15: Plagioclase Minor and Trace Elements for each sample. Mean calculated from data above limits of detection (LOD). “n” represents number of data above LOD. “N” represents number of analysed samples. “ σ ” represents standard deviation.

	1.AS (N=36)				1(B)MP (N=44)				1.AS.H (N=35)			
	mean	n	σ	mean LOD	mean	n	σ	mean LOD	mean	n	σ	mean LOD
Li	14.11	5	10.64	1.36	4.57	2	2.77	1.39	3.98	19	2.87	1.18
Mg	2398.51	7	2459.35	63.86	20.23	3	21.69	3.57	391.40	6	872.93	9.20
Ti	419.62	11	683.87	23.01	13.26	1	0.00	7.12	243.53	3	323.23	9.56
Mn	26.49	34	62.70	3.89	4.14	27	4.03	1.40	5.37	11	6.52	1.30
Zn	50.07	7	36.12	17.07	44.38	2	14.67	23.11	13.74	21	5.81	7.79
Rb	27.26	9	33.48	1.19	1.86	1	0.00	0.47	22.79	1	0.00	0.35
Sr	740.87	36	109.44	64.91	504.79	44	69.59	54.22	937.19	35	103.26	89.73
Y	0.30	9	0.23	0.07	0.21	5	0.18	0.07	0.00	13	0.00	0.00
Cs	2.68	4	1.12	0.25	-	0	-	0.30	1.40	1	0.00	0.13
Ba	51.04	36	41.63	5.91	61.61	44	20.41	7.53	20.46	35	8.24	3.08
La	0.27	25	0.57	0.05	1.01	37	0.87	0.15	0.00	15	0.00	0.00
Ce	0.41	30	0.89	0.08	1.30	39	1.29	0.18	0.00	19	0.01	0.00
Pr	0.05	17	0.10	0.01	0.17	25	0.10	0.03	0.00	17	0.00	0.00
Eu	0.61	28	0.52	0.10	0.70	40	0.35	0.16	0.03	30	0.03	0.02
Pb	33.84	36	5.42	3.26	22.54	44	5.78	2.76	46.54	35	4.56	4.69

5.3.2 Muscovite

Muscovite is an important host of many minor and trace elements in systems involving crustal melting and metamorphism. Relative to other pegmatites, particularly those of economic potential, Li is depleted in the muscovites of the Mataketake region. Interestingly, the pegmatite is depleted relative to the adjacent schist. The average muscovite in 1.AS contains 46.4ppm Li ($n=44$, $\sigma=5.5\text{ppm}$), compared to 40.6ppm Li in 1(B)MP ($n=45$, $\sigma=5.23\text{ppm}$). Mn also records depletion in 1(B)MP compared to 1.AS (Figure 5.9). Figure 5.9 appears to show a positive correlation between Mn and Li. Muscovites from 1(B)MP are depleted in Sc, relative to 1.AS (Figure 5.9), with average Sc quantities of 39.2ppm ($n=45$, $\sigma=15.3\text{ppm}$) and 52.0ppm ($n=44$, $\sigma=18.0\text{ppm}$) respectively. Vanadium and chromium are also depleted in muscovite from the pegmatite; with average V of 0.68ppm ($n=31$, $\sigma=0.44\text{ppm}$) and all Cr below LOD (average LOD=3.03ppm) in 1(B)MP, but with average concentrations of 291ppm V ($n=44$, $\sigma=75.4\text{ppm}$) and 149ppm Cr ($n=44$, $\sigma=55.5\text{ppm}$) in 1.AS (Figure 5.9). V and Cr are preferentially hosted in the octahedral site in muscovite (Fischer, 1973; Heinrich & Levinson, 1955; Imai et al., 1980; Kelley et al., 2017; Viswanathan et al., 2012). Figure 5.9 shows Al(VI) against V and Cr individually, communicating the substitution of these elements into the octahedral site. There is argument for correlation between Al(VI) and V and Cr in 1.AS. Co is hosted in lesser quantities than the aforementioned elements; 1.AS averages 2.61ppm Co ($n=44$, $\sigma=0.80\text{ppm}$), whereas 1(B)MP averages 1.11ppm Co ($n=42$, $\sigma=0.28\text{ppm}$). Zn quantities are indistinguishable between the two lithologies; both averaging 78-79ppm Zn (1.AS: $n=44$, $\sigma=21.4\text{ppm}$, 1(B)MP: $n=45$, $\sigma=18.2\text{ppm}$). 1(B)MP hosts more Ga, averaging 69.5ppm ($n=45$, $\sigma=7.36\text{ppm}$), compared to an average of 62.0ppm Ga for 1.AS ($n=44$, $\sigma=6.0\text{ppm}$).

For LILE (Pb, Sr, Ba, K, Rb, Cs), apart from K, Ba is hosted in the greatest quantity and is enriched in the pegmatite relative to the schist, averaging 3164ppm Ba in 1(B)MP ($n=45$, $\sigma=674.6\text{ppm}$), compared to 2607ppm Ba in 1.AS ($n=44$, $\sigma=683.2\text{ppm}$). Other LILE show a different pattern, with K, Rb, Cs and Pb being depleted in 1(B)MP relative to 1.AS (Table 5.16). Sr shows negligible change between muscovites of the two lithologies.

Table 5.16: Muscovite minor and trace element composition. Mean calculated from data above limits of detection (LOD). “n” represents number of data above LOD. “N” represents number of analysed samples. “σ” represents standard deviation.

	1.AS (n=44)				1(B)MP (n=45)			
	<i>mean</i>	<i>n</i>	<i>stdev</i>	<i>mean LOD</i>	<i>mean</i>	<i>n</i>	<i>stdev</i>	<i>mean LOD</i>
Li	46.37	44	5.52	5.13	40.63	45	5.23	5.33
Ca	1960.67	2	719.59	709.04	1932.09	1	0.00	679.91
Sc	51.97	44	17.95	3.62	39.15	45	15.30	3.72
Ti	2959.30	44	1024.63	0.44	1029.93	45	360.82	0.44
V	291.25	44	75.35	0.34	0.68	31	0.44	1.71
Cr	148.83	44	55.52	3.04	-	0	-	3.03
Mn	136.19	44	27.17	2.27	111.21	45	17.10	2.30
Co	2.61	44	0.80	0.47	1.11	42	0.28	0.53
Zn	78.85	44	21.39	21.50	78.12	45	18.17	22.44
Ga	61.95	44	6.02	0.21	69.45	45	7.36	0.25
Rb	250.88	44	25.59	1.69	227.57	45	25.75	1.86
Sr	30.04	44	10.88	0.05	30.96	45	4.46	0.06
Y	0.12	19	0.07	0.08	0.11	15	0.04	0.10
Zr	1.24	44	0.74	0.05	1.23	44	0.67	0.05
Nb	27.81	44	12.12	0.05	26.91	45	8.91	0.06
Cs	2.85	44	0.86	0.68	1.15	27	0.38	0.73
Ba	2607.41	44	683.15	0.05	3164.11	45	674.61	0.21
La	0.02	39	0.01	0.01	0.03	36	0.06	0.00
Ce	0.003	22	0.004	0.002	0.005	18	0.013	0.003
Pr	0.001	18	0.001	0.007	0.001	20	0.001	0.004
Yb	0.05	35	0.03	0.01	0.02	25	0.02	0.01
Pb	7.60	44	1.31	0.56	4.16	45	1.53	0.52

Of the analysed HFSE (Ti, Y, Zr, Nb, La), Ti is the only element that changes substantially; with a mean average of 1030ppm Ti in 1(B)MP (n=45, σ =360.8ppm), compared to 2959ppm Ti in 1.AS (n=44, σ =1025ppm). Most Y data is below LOD. Zr shows no notable change between 1.AS and 1(B)MP; with an average muscovite content of 1.2ppm. Nb also shows no significant change (27.8ppm 1.AS (n=44, σ =12.1ppm), 26.9ppm 1(B)MP (n=45, σ =8.91ppm)). La values are all very low, averaging 0.023ppm for 1.AS (n=39, σ =0.010ppm), with 5 below LOD (average LOD=0.006ppm), and 0.028ppm for 1(B)MP (n=36, σ =0.064ppm), with 9 below LOD (average LOD=0.003ppm).

There is negligible Ce and Pr within the analysed muscovites, with most data below LOD. As such, the analysed LREE (La, Ce, Pr), are all depleted in the muscovites of the Mataketake region. Yb is also depleted within muscovites, with many data below LOD. Sc is the only REE to be hosted in significant quantities.

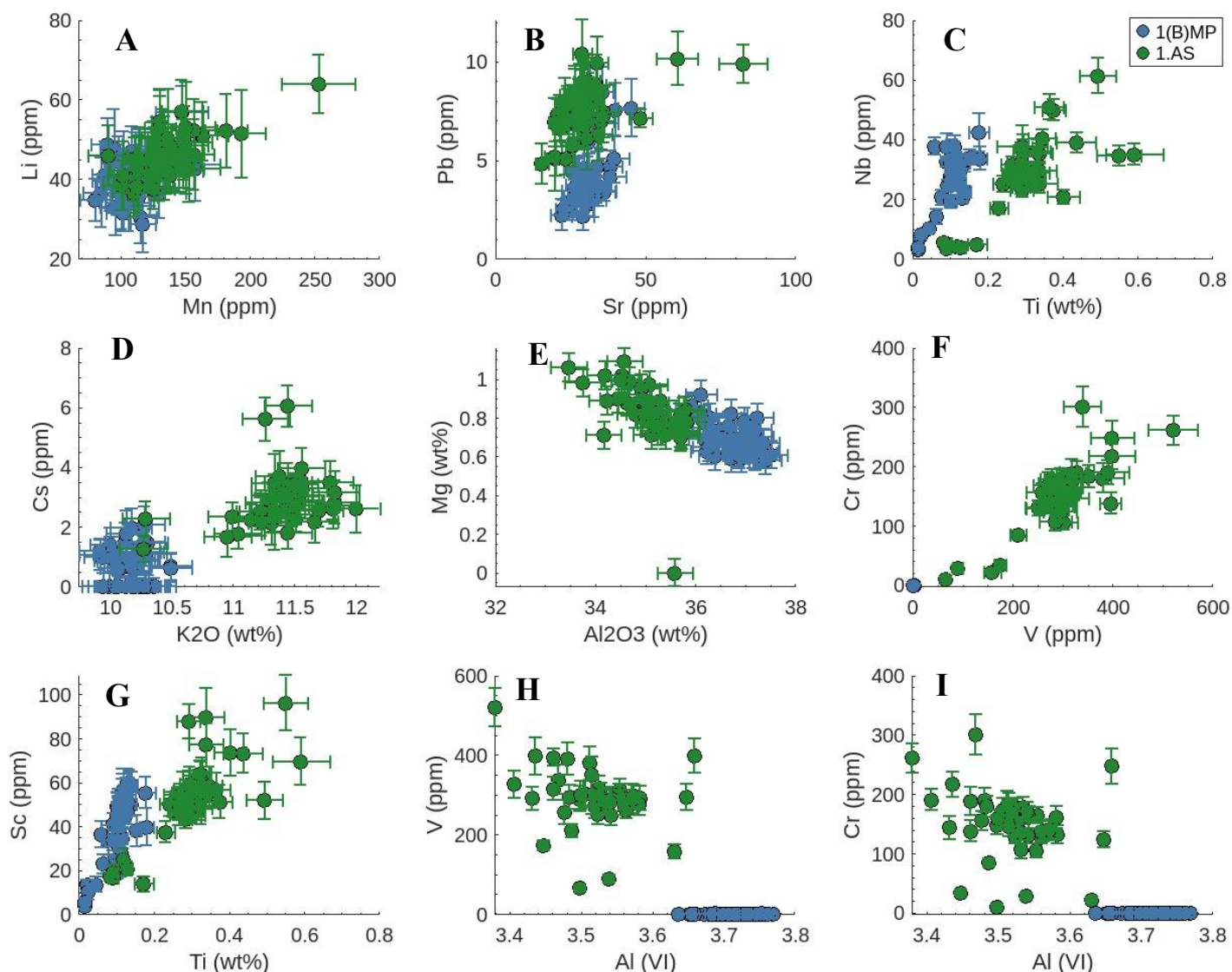


Figure 5.9: Muscovite geochemistry, showing 2 distinct compositions. **A:** Mn (ppm) v Li (ppm) showing positive correlation. **B:** Sr (ppm) v Pb (ppm); no variation in Sr, but Pb shows 2 discrete groups. **C:** Ti (wt%) v Nb (ppm). **D:** K₂O (wt%) v Cs (ppm); generally 2 distinct groups, although a few 1.AS muscovites are contained with 1(B)MP. **E:** Al₂O₃ (wt%) v Mg (wt%). **F:** V (ppm) v Cr (ppm); a positive correlation, note how all 1(B)MP muscovite based around 0,0; LOD for V and Cr are 0.26ppm and 1.58ppm respectively. **G:** Ti (wt%) v Sc (ppm). **H:** Al (VI) v V (ppm); perhaps a negative correlation for 1.AS. **I:** Al(VI) v Cr (ppm); apparent negative correlation for 1.AS.

5.3.3 Biotite

The crystal structure of biotite group minerals facilitates the incorporation of many minor and trace elements with varying ionic sizes and charges (Gao et al., 2023; Mohammadi et al., 2021; Tischendorf et al., 2007; Tischendorf et al., 2004). The tetrahedral sheet can hold Si, Al, Fe, B and Be (Tischendorf et al., 2007). Al, Fe, Mg, Mn, Cr, V and Li are hosted in the octahedral site (Tischendorf et al., 2007; Tischendorf et al., 2004). Whereas, K, Na, Rb, Cs, Ca and Ba can be hosted in the interlayer, and the hydroxyl site can also host anions of F, Cl, S, O (Tischendorf et al., 2007). Biotite is crucial in dictating Li abundances in melting scenarios (Kunz et al., 2022). Li is relatively depleted in all biotite samples (when considering it is a preferred host), relative to economic concentrations; for

example, the enriched G5 Cornubian granite (Cornwall, UK) averages whole-rock abundances of 1363ppm (Simons et al., 2017). Biotite from 1(B)MP is slightly enriched in Li relative to 1.AS; 1(B)MP averages 177ppm Li ($n=33$, $\sigma=18.8$ ppm), 1.AS averages 166ppm Li ($n=32$, $\sigma=15.2$ ppm), and 1.AS.H averages 244ppm Li ($n=41$, $\sigma=22.5$ ppm). Na is depleted in the pegmatite (~500ppm average ($n=33$, $\sigma=144.7$ ppm)), compared to the schists (averaging ~690ppm 1.AS ($n=32$, $\sigma=384.8$ ppm), ~760ppm 1.AS.H ($n=41$, $\sigma=187.7$ ppm)). Scandium is interesting, in that the distal 1.AS.H averages the greatest abundances (43ppm ($n=41$, $\sigma=7.9$ ppm)), and 1.AS averages the lowest (15ppm ($n=32$, $\sigma=5.4$ ppm)). 1(B)MP averages 21ppm Sc ($n=33$, $\sigma=2.2$ ppm). This indicates that Sc is likely principally controlled by factors other than melting.

Ti abundances are generally greater in 1(B)MP (average 2.2 wt% oxide ($n=33$, $\sigma=0.28$ wt%)), than the Alpine Schist samples (average 1.8wt% oxide (1.AS ($n=32$, $\sigma=0.31$ wt%)). TiO₂ contents are generally contained in the range of 1.5-2.5wt%, with pegmatite biotite ranging from 1.7-2.9wt% TiO₂, which is lower than ranges associated with magmatic biotite (Feng et al., 2021; Henry et al., 2005; Patiño Douce & Harris, 1998; Stussi & Cuney, 1996). This indicates biotite is not of magmatic origin, which is expected for a low temperature partial melt in a metamorphic setting.

Table 5.17: Biotite minor and trace element composition. Mean calculated from data above limits of detection (LOD). “n” represents number of data above LOD. “N” represents number of analysed samples. “σ” represents standard deviation.

	1.AS (N=32)				1(B)MP (N=33)				1.AS.H (N=41)			
	mean	σ	n	mean LOD	mean	σ	n	mean LOD	mean	σ	n	mean LOD
Li	165.71	15.18	32	22.81	177.18	18.76	33	22.02	244.16	22.49	41	27.94
Na	691.55	384.84	32	120.51	501.24	144.74	33	99.22	762.43	187.74	41	136.43
Ca	605.96	453.79	11	165.91	173.13	59.23	22	162.19	531.49	402.59	10	162.79
Sc	15.22	5.39	32	2.82	20.78	2.23	33	3.45	42.68	7.88	41	6.02
V	368.98	165.49	32	45.59	4.85	5.48	33	0.69	469.63	117.65	41	46.58
Cr	220.77	106.84	32	25.18	4.69	0.00	1	2.08	107.88	59.73	41	11.67
Mn	1841.94	207.90	32	262.45	1722.86	146.00	33	190.42	286.64	74.58	41	34.48
Zn	546.75	44.23	32	91.82	593.29	55.03	33	86.36	511.12	49.85	41	79.18
Ga	34.07	4.40	32	3.66	36.57	2.82	33	3.66	40.53	3.69	41	3.88
Rb	431.59	76.85	32	61.93	452.99	32.90	33	48.29	435.48	31.01	41	48.68
Sr	2.37	4.69	32	0.51	0.84	0.48	32	0.27	2.77	7.11	41	0.87
Y	0.69	2.43	27	0.16	0.18	0.32	28	0.10	0.49	1.81	29	0.12
Zr	4.68	20.29	21	0.71	0.07	0.10	25	0.07	25.51	64.32	29	7.70
Nb	20.70	10.89	32	2.29	44.96	9.11	33	4.35	31.59	6.24	41	3.17
Sn	1.77	0.84	32	0.32	2.30	0.25	33	0.37	6.25	0.68	41	0.74
Cs	20.37	3.09	32	2.48	12.43	5.84	33	1.53	27.03	3.35	41	3.15
Ba	985.78	156.01	32	128.07	1149.96	190.34	33	132.67	901.37	118.17	41	110.75
La	4.3	25.00	25	0.58	0.02	0.03	29	0.01	0.31	1.65	41	0.07
Yb	0.05	0.14	20	0.01	0.01	0.01	19	0.01	0.09	0.22	41	0.04
W	0.14	0.08	32	0.06	0.06	0.05	32	0.04	0.33	0.07	41	0.10
Pb	3.19	1.14	32	0.57	3.78	0.50	33	0.62	7.09	1.84	41	0.97

Biotites in 1(B)MP have negligible Cr, with most data below detection limits (Figure 5.10). Biotites in 1.AS average ~221ppm Cr ($n=32$, $\sigma=106.8$ ppm), and ~108ppm Cr ($n=41$, $\sigma=59.7$ ppm) in 1.AS.H. Likewise, V is depleted in 1(B)MP, although all data is within detection limits, whilst biotite within the schist samples attains much higher V. The average concentrations are displayed in Table 5.17.

Mn is significantly lower in biotites from 1.AS.H (averaging 287ppm ($n=41$, $\sigma=74.6$ ppm)) compared with the biotites in the Mataketake region: 1723ppm (1(B)MP ($n=33$, $\sigma=146.0$ ppm)), and 1842ppm (1.AS ($n=32$, $\sigma=207.9$ ppm)). Zn is elevated in 1(B)MP relative to the schist samples.

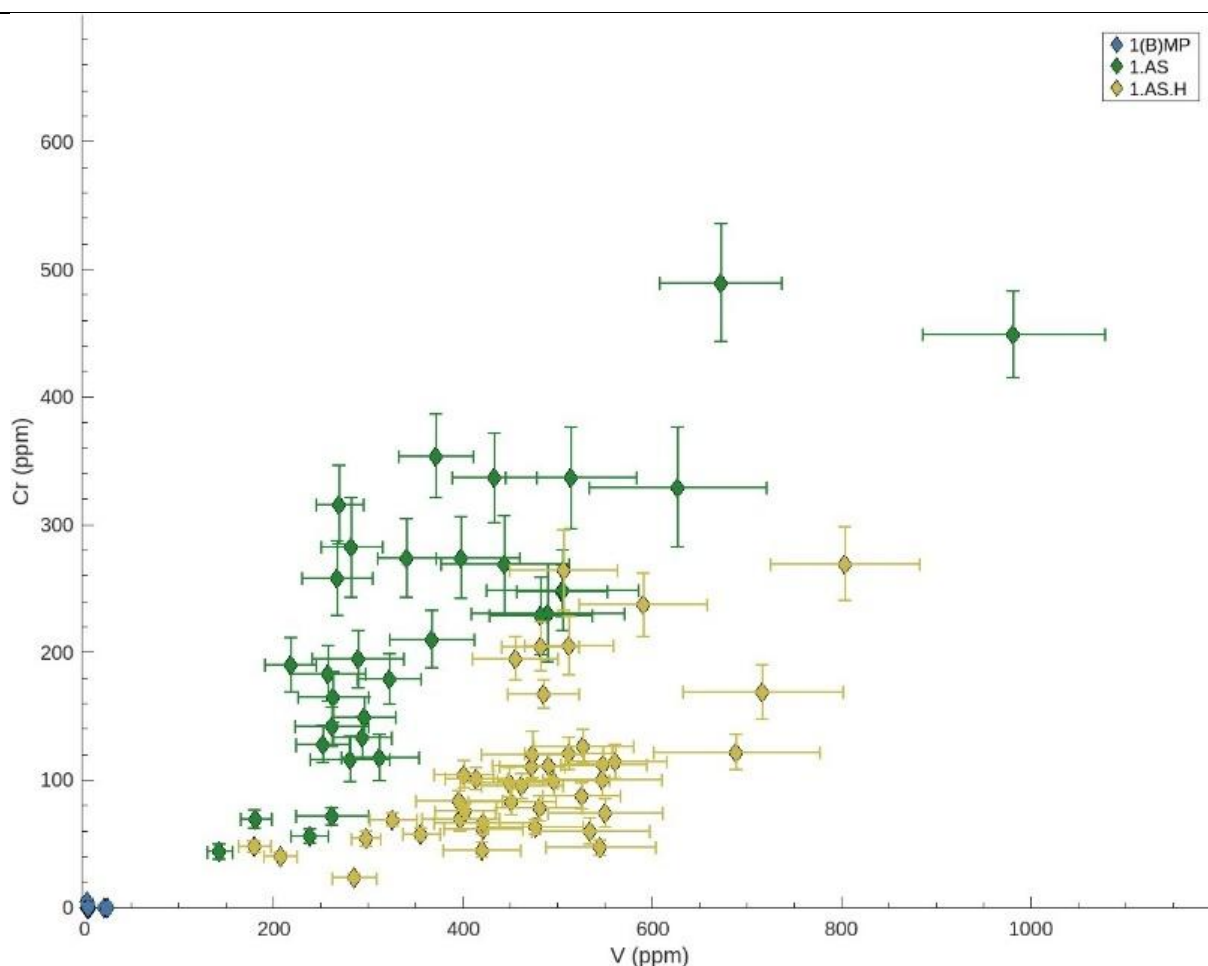


Figure 5.10: V (ppm) v Cr (ppm) within biotite. All data from Laser-ICP-MS. Detection limits for V and Cr average 0.69ppm and 2.08ppm for 1(B)MP respectively. Uncertainty for ICP Data (V , Cr) is 2SE.

There is little variation in Ga abundances, with average concentrations of 36.6ppm, 34.1ppm, and 40.5ppm in 1(B)MP ($n=33$, $\sigma=2.8$ ppm), 1.AS ($n=32$, $\sigma=4.4$ ppm) and 1.AS.H ($n=41$, $\sigma=3.7$ ppm) in turn.

Rb is slightly enriched in the pegmatite, with an average of 453ppm ($n=33$, $\sigma=32.9$ ppm), compared to averages of 432ppm and 436ppm in 1.AS ($n=32$, $\sigma=76.8$ ppm) and 1.AS.H ($n=41$, $\sigma=31.0$ ppm) respectively. Sr is depleted in all biotite, with most samples attaining concentrations <2 ppm. There are a few outliers, with the highest recorded concentration achieving 25ppm Sr (1.AS). This is unlikely to be due to crossover with another phase, mineral inclusions, fluid inclusions etc, because other

elements achieve normal concentrations. Of the LILE, Ba is the most enriched in the micas (excluding K). Within biotite, Ba averages 1150ppm, 986ppm and 901ppm in 1(B)MP ($n=33$, $\sigma=190.3$ ppm), 1.AS ($n=32$, $\sigma=156.0$ ppm) and 1.AS.H ($n=41$, $\sigma=118.2$ ppm) respectively. Cs and Pb are enriched in 1.AS.H relative to the Mataketake region biotites, with average Cs concentrations of 12.4ppm (1(B)MP ($n=33$, $\sigma=5.8$ ppm)), 20.4ppm (1.AS ($n=32$, $\sigma=3.1$ ppm)), 27.0ppm (1.AS.H ($n=41$, $\sigma=3.4$ ppm)), and average Pb concentrations of 3.8ppm (1(B)MP ($n=33$, $\sigma=0.5$ ppm)), 3.2ppm (1.AS ($n=32$, $\sigma=1.1$ ppm)), and 7.1 ppm (1.AS.H ($n=41$, $\sigma=1.8$ ppm)).

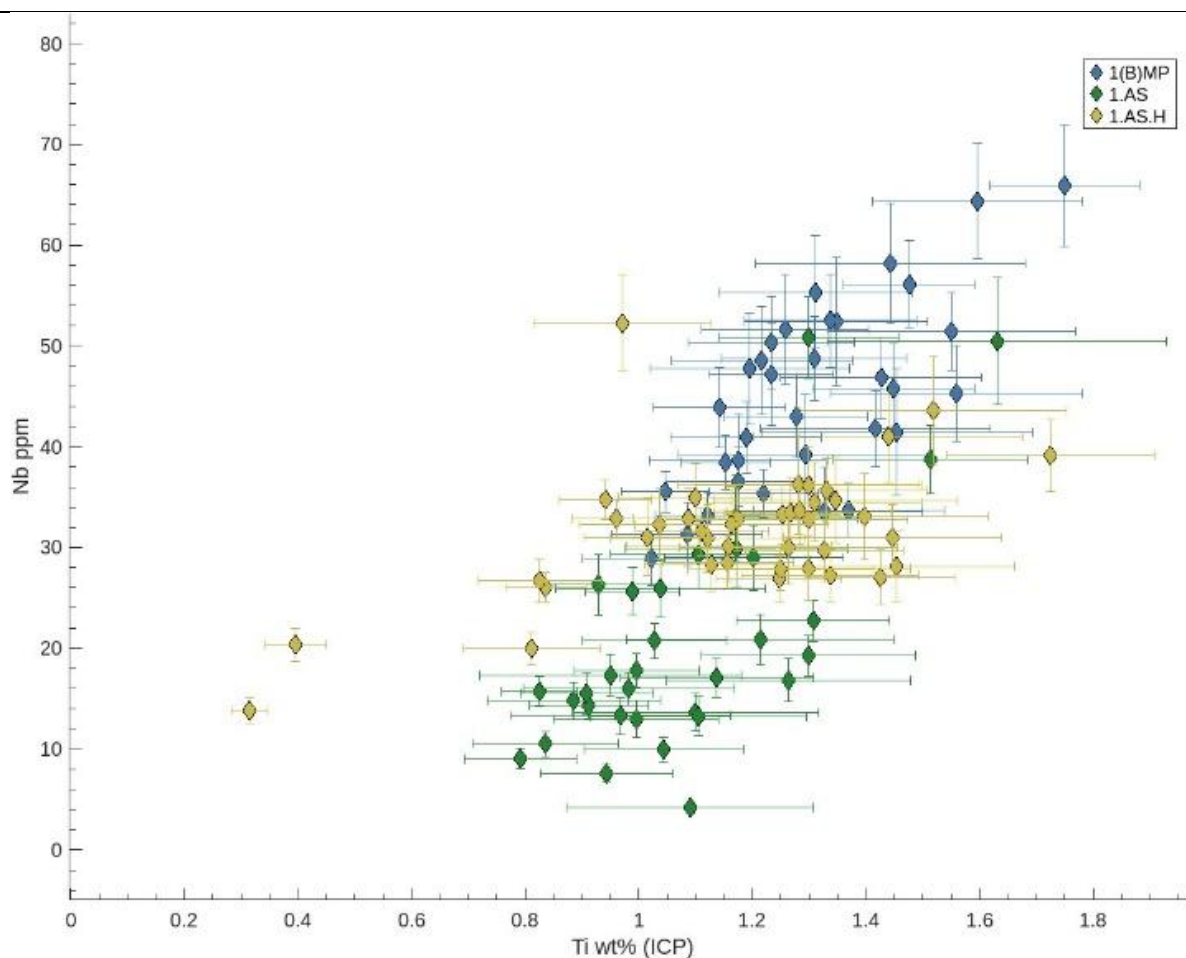


Figure 5.11: Ti wt% v Nb ppm in biotite grains.

Of the analysed HFSE (Ti, Y, Nb, Zr, La, W), Ti and Nb are the most abundant in biotite. 1(B)MP has significantly more Nb than 1.AS; it averages over twice the mean average for 1.AS (45ppm (1(B)MP ($n=33$, $\sigma=9.1$ ppm)), 21ppm (1.AS ($n=32$, $\sigma=10.9$ ppm))). Nb is a key HFSE and can easily substitute for Ti in Ti-bearing minerals. There is good correlation between Nb and Ti (Figure 5.11). Zirconium values are generally negligible, with many recording concentrations below LOD. La concentrations are generally <0.01 ppm, with some data below detection limits. The existence of some elevated Zr and La abundances highlights possible uncertainties/limitations to the analysed samples. These outliers are likely sourced from crossover with accessory phases/inclusions of accessory phases and grain-scale fractures. Upon review of sample locations, there is no distinct evidence for crossover with other phases. However, the observed ‘slippage’ along mica cleavage planes, and the shearing of

micas, results in opportunity for impurities along cleavage planes/fractures. These datapoints are kept, as other than Zr and La, the elemental data aligns with other biotite values. Furthermore, there is no sample point Zr is elevated, and La is elevated. Y are nearly all <1ppm, with many below LOD. Yb quantities are negligible in all 3 rock samples, with Yb in biotite often occurring below detection limits. 1(B)MP averages the least W, at 0.06ppm ($n=33$, $\sigma=0.05\text{ppm}$). Whereas 1.AS.H averages the most, at 0.33ppm W ($n=41$, $\sigma=0.07\text{ppm}$). 1.AS averages 0.14ppm W in biotite ($n=32$, $\sigma=0.08\text{ppm}$). Sn varies mainly with location, with 1.AS.H averaging 6.2ppm ($n=41$, $\sigma=0.7\text{ppm}$). 1(B)MP averages 2.3ppm ($n=33$, $\sigma=0.2\text{ppm}$), and 1.AS averages 1.8ppm ($n=32$, $\sigma=0.8\text{ppm}$).

5.4 Limitations – Input into methods.

There are limitations to the accuracy of produced phase maps, which were used to quantify mineralogical composition. Firstly, there are 5 phase maps from 1.AS, covering a total of 2,873,444 pixels ($9,528,780\mu\text{m}^2$), and 4 Phase maps from 1(B)MP, covering 21,005,274 pixels ($69,656,703\mu\text{m}^2$). As such, although these provide a good estimate, they do not absolutely quantify the phase abundances. Secondly, the phase maps in 1(B)MP cover more area, likely resulting in mineralogical composition being more accurately reflected. In lithologies where phase banding is observed, map location may alter calculated mineral quantification.

When Phase Mapping, Grouping Level, Binning Factor, and Boundary Tolerance were manually decided in Aztec so that the volume of ‘Unassigned Pixels’ were minimised. However, it is impossible to completely remove these Unassigned Pixels, and therefore uncertainty is introduced. The first concern is the perimeter of grains relative to grain sizes. Phases that occur as smaller grains are generally not grouped/identified to the same relative accuracy, due to a higher perimeter:grain-size ratio, and instead they often comprise a significant proportion of the ‘Unassigned Pixels’. Within the major phases, an example would be micas. As the micas form anastomosing, decussate/foliated textures, due to smearing along their 001 plane, and recrystallisation, they commonly form aggregates with ‘shards’ of biotite. These finer grains of biotite are not identified to the same extent as the muscovites in the muscovite-dominated aggregates. To reduce the inaccuracy in produced estimates, FIJI (ImageJ) was used to differentiate biotite from muscovite, as they attain differing grayscale values within produced electron images. This process is outlined in the Methods section (Section 3). Another limitation with phase mapping, is the pixel size relative to grain size. Pixel size results in uncertainty and will contribute to the total quantity of ‘Unassigned Pixels’. For smaller grains, such as micas and minor phases (titanite, epidote, ilmenite etc.), the grain-size:pixel-size ratio is smaller, compared to plagioclase. These introduce uncertainty in the quantification of mineral abundances. This uncertainty was reduced for micas, using FIJI (ImageJ). For the 4 main phases, we doubt these uncertainties will affect phase quantities to any significant extent. However, the uncertainties will disproportionately affect minor phases.

There is uncertainty within EDS data. This is made clear by the two biotite compositions for 1(B)MP, which are disparate to the Laser-ICP data, which shows a more continuous compositional variation (see 4.2.3). Although EDS uncertainty is generally quantified with σ values, this error is different. These data were all collected on X date, and are thought to represent either human error (e.g., reduced Acquisition Time), or are simply reflecting uncertainty within SEM-EDS. Either way, the composition can still be confined to the given range of values; the main limitation with this error is that it does not allow for direct comparison with 1.AS. In general, the σ values incorporate the associated error and allow statistical analysis.

Laser-ICP data also attains its own uncertainty. The uncertainty for a given reading is the 2-Standard-Error value (2SE). Within all figures, ICP error bars are given as $\pm 2SE$ (total error bar length = 4SE). The slit size for all ablation was 40x40 μm , which is less than the norm of 50x50 μm . This reduced slit size introduces uncertainty, however this could not be avoided, as the fine-grained nature of many grains meant that 40x40 μm was the largest slit size that allowed sufficient samples to be collected. The depth profile and surface roughness also introduce uncertainty in Laser-ICP-MS. As the laser ablates material layer by layer this results in progressively less counts-per-second (CPS) with each laser pulse, as the ablation efficiency decreases due to changing surface morphology and the reduced availability of material at depth. The high sensitivity associated with LA-ICP-MS makes it useful for trace element analyses. However, the precision for some trace elements can vary, and for elements close to detection limits, associated error may negate statistical significance. This error is rather unavoidable, however, elements that were deemed more important (e.g., Li) were counted at the start.

Within LA-ICP there is also uncertainty concerned with contamination and grain overlap from adjacent phases. This is pertinent due to the texture of samples. Post-emplacement shearing has led to 'smearing' along mica 001 planes, lattice deformation in all grains (strained quartz, bookshelf fracturing of plagioclase porphyroblasts, deformation extinction etc.), as well as other textural context that heightens risk of contamination and/or grain crossover. Where obvious contamination/inclusions/fractures were present, this was avoided. However, the nature of these rocks means that this error simply reflects their geological history.

Limitations in LA-ICP-MS were managed on the most part through careful sample preparation and the use of internal standards from SEM-EDS to calibrate data, and external standards to compare against (NIST610, NIST612, BHVO, BCR, StHS). The use of internal standards assumes SEM-EDS is accurate. However, this may not be the case, as SEM-EDS does not identify trace elements, and therefore major element abundances can be elevated.

6 DISCUSSION

Here we discuss all evidence from the previous chapters that may aid in determining the processes behind the formation of the Mataketake Pegmatites, this is done with the view to why the Mataketake Pegmatites are not enriched in metals such as Li. Initially we discuss basic geochemical observations, including changes in mineralogical abundances between the schist and pegmatite, as well as major and trace element variation (6.1.1). We constrain formation temperatures, using titanium contents in biotite (6.1.2). We consider these results for temperature relative to existing thermometry in the region. We use geochemical data to infer melting processes in 6.1.1 and 6.1.3.1, this includes calculated whole-rock and normative whole-rock compositions. In 6.1.3.2 we model melt contents for K, Fe and Mg to constrain melting proportions of key phases, as well as trace elements (Sr, Ba, Pb, La and Li) with the intent to constrain melting reactions. 6.1.3.3 covers the limitations within this geochemical modelling before 6.1.4 summarises proposed melting reactions and processes. Finally, we link this to metal enrichment, building on previous literature (6.2).

6.1 Formation of Mataketake Pegmatites

6.1.1 Basic Geochemical Observations

6.1.1.1 Mineralogical Abundances and Major Elements

Chapter 5 of this thesis outlines geochemical observations. Within this subsection we discuss their implications. In section 5.1, we note the changes in mineralogical abundances between 1.AS (assumed protolith), and the pegmatite. Notably, the pegmatite is comprised of slightly more quartz (39.15% compared to 37.98%), and significantly more plagioclase (33.50% compared to 22.52%) than the schist. Conversely, there is a reduction in the quantity of muscovite from the schist to the pegmatite (19.41% in the pegmatite compared to 24.15% in the schist) and biotite (7.58% compared to 13.50%). These four phases make up ~98% of 1.AS and >99% of 1(B)MP. Assuming that the Alpine Schist sample is representative of the parental rock to the pegmatite, this indicates that a lesser proportion of mica has contributed to the melt than plagioclase. A key difference between fluid-present and fluid-absent melting of muscovite is that in fluid-absent dehydration melting, H₂O is supplied by muscovite during incongruent breakdown, and as such is consumed to a greater extent than plagioclase (Patiño Douce & Harris, 1998). In comparison, plagioclase is consumed in greater proportions than muscovite during fluid-fluxed muscovite melting (Patiño Douce & Harris, 1998; Scaillet & Pichavant, 2024). This is because the plagioclase + quartz solidus is depressed with increasing H₂O activity to a greater extent than it affects mica stability (Patiño Douce & Harris, 1998). Patiño Douce and Harris (1998) highlight how temperature and pressure affect the relative consumption of plagioclase and muscovite during fluid-fluxed melting. Their experimental work at 2wt% H₂O, P = 6kbar, and T = 750°C and 775°C shows greater muscovite proportions reacting out at higher temperatures (Patiño Douce &

Harris, 1998). To the contrary, lower temperatures and higher pressures are more conducive to plagioclase consumption (Patiño Douce & Harris, 1998). As such, the compositional variation in this study is indicative of H₂O-fluxed muscovite melting at low-T.

Major element analyses of plagioclase revealed distinct changes in feldspar compositions from the schist to the pegmatite (Table 5.13 & Figure 5.1). Plagioclase compositions within the pegmatite averages An_{18.1}, with a standard deviation of 1.3. This is much more albitic than the Alpine Schist, with plagioclase compositions in 1.AS averaging An_{28.1}, (standard deviation of 6.5), and in 1.AS.H averaging An_{22.6}, (standard deviation of 2.5). The varying standard deviations also tell a story of the plagioclase in the pegmatite being much more confined in compositional range (Figure 5.1). This communicates that the plagioclase within the pegmatite cover a distinct, confined range of compositions, which we infer as indicating precipitation from melt. The purely metamorphic feldspars of the Alpine Schist have had greater opportunity to attain varying compositions due to their prolonged metamorphic history (see Chapter 2).

Muscovites also display unique compositions for the pegmatite compared to the schist (Figure 5.3, 5.4); with the muscovites in the schist demonstrating more phengitic compositions. As the Alpine Schist sample 1.AS is from the same rock specimen as Mataketake Pegmatite sample 1(B)MP, we interpret this to mean that pegmatitic muscovites precipitated from the melt, producing a distinct composition. Between 1.AS and 1(B)MP, it is more difficult to comment on the extent to biotite precipitation from melt. Biotite from 1(B)MP appears as two distinct compositional clusters in terms of major element concentrations (e.g., Al, Fe, Mg) (Figure 5.5, 5.6 & 5.7). These two clusters straddle the two compositional extremes of 1.AS. We attribute these two groupings to analytical uncertainty due to detection limits associated with SEM-EDS (Section 5.2.3).

6.1.1.2 Trace Elements

Within plagioclase, trace elements Sr, Pb and Ba display the most significant trend, with distinct compositions for each rock sample. Figure 5.8 displays the three compositions, with 1.AS and 1(B)MP always forming two distinct clusters. Within plagioclase grains, both Sr and Pb are depleted in the pegmatite relative to the schist, whereas Ba is enriched in the pegmatite. For Sr, observed depletion is consistent with changes in partitioning behaviour due to lower X_{An} in the pegmatite, however this is not the case for Ba (Blundy & Wood, 1991). This therefore suggests something other than a change in partitioning due to lower anorthite content in plagioclase within pegmatite, perhaps a change in melt composition. These unique compositions inform us of the melt origins of the plagioclase in pegmatites. The proximity of 1.AS and 1(B)MP (same hand specimen), means that trace element variation cannot be attributed to processes post-crystallisation, and therefore it is concluded that trace-element variation is due to plagioclase in 1(B)MP precipitating from melt. Table 5.15 shows how Rb averages 27.3 ppm within plagioclase of 1.AS ($n=9$, $\sigma = 33.5$, mean LOD = 1.2

ppm), whereas 1(B)MP only has one datapoint where Rb is above detection limits, at 1.86 ppm (mean LOD = 0.47ppm). Consequently, plagioclase in the Mataketake Pegmatites are Rb-poor relative to the schist .

Weinberg and Hasalová (2015) highlight how Sr, Rb and Ba can indicate melting reactions as their concentrations are dictated by major minerals, as suggested by the analysis above. For those major minerals, plagioclase is typically Sr-enriched and Rb-poor, whereas micas are Rb-enriched and Sr-poor (Inger & Harris, 1993; Weinberg & Hasalová, 2015). Consequently, water-fluxed melting has a low Rb/Sr ratio, whereas mica-dehydration reactions have high Rb/Sr ratios (Weinberg & Hasalová, 2015). This is due to water-fluxed melting depressing the quartz + plagioclase solidus, whilst micas remain stable for longer, thus liberating more Sr than Rb as plagioclase dominates the melting fraction. Conversely, mica-dehydration melting reactions involve the consumption of micas early on, enriching the melting fraction in Rb, as well as liberating H₂O from the hydroxyl site. Inger and Harris (1993) show how Rb/Sr varies with Sr and Ba during varying melting reactions. Briggs and Cottle (2018) utilised this to infer melting reactions for the Mataketake Pegmatites by plotting their data on a Ba v Rb/Sr plot (Figure 6.1). This study has built on this by providing new data for Ba v Rb/Sr for the Alpine Schist and Mataketake Pegmatite. To do this, whole-rock compositions were estimated from modal analysis combined with the trace element data for Sr, Rb and Ba within plagioclase, muscovite and biotite, with the assumption that quartz holds negligible quantities of these elements. This analysis shows that the pegmatite (1.B.MP) has lower Ba and slightly lower Rb/Sr than the schist (1.AS). Figure 6.1 therefore aligns with most data from Briggs and Cottle (2018); with a reduction in Ba contents in the pegmatite relative to the schist, whilst Rb/Sr does not increase, therefore suggesting H₂O-present muscovite dehydration melting. Uncertainties in this calculation are dominated by the range of compositions analysed. Average uncertainties as a percentage of average composition for each phase are contained in Table 6.1. Standard deviations are approximately 10-15% relative, except for Rb in plagioclase (4% in 1.AS and 25% in 1(B)MP) and Sr in biotite (21% and 32% for 1.AS and 1(B)MP respectively). Biotite represents 13.5% of 1.AS and 7.6% of 1(B)MP, and therefore these high percentage uncertainties may have affected the accuracy of these whole-rock calculations. However, with sample sizes of 33 and 32 analyses for biotite in the pegmatite and schist, we expect the effects of the uncertainty to be limited because the mean is well constrained. For Rb, plagioclase represents 33.5% of the pegmatite, and therefore an uncertainty of 25% may have increased inaccuracy with whole-rock compositional abundances for Rb.

Table 6.1: Average uncertainties as a percentage of average composition for Sr, Rb and Ba

Phase		Sr	Rb	Ba
Plagioclase	1.AS	9%	4%	12%
Plagioclase	1(B)MP	11%	25%	12%
Muscovite	1.AS	12%	12%	12%
Muscovite	1(B)MP	13%	12%	13%
Biotite	1.AS	21%	14%	13%
Biotite	1(B)MP	32%	11%	12%

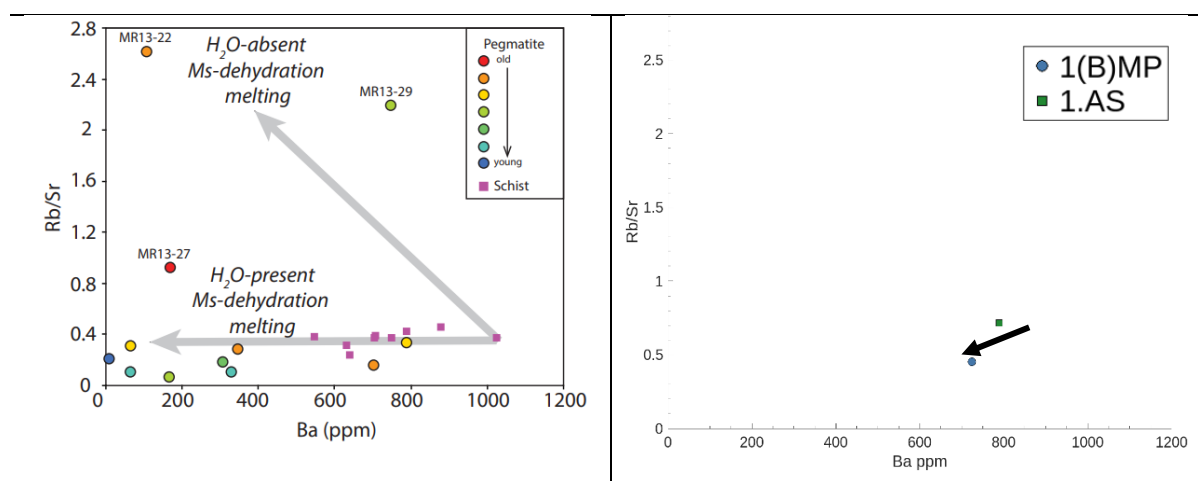


*Figure 6.1: **Left:** Briggs and Cottle (2018), showing whole rock compositions of Ba (ppm) against Rb/Sr for the Alpine Schist and Mataketake Pegmatites. **Right:** This Study, showing whole rock compositions of Ba (ppm) against Rb/Sr for the Alpine Schist and Mataketake Pegmatite. Arrow shows compositional change from 1.AS to 1(B)MP – indicative of H₂O-present muscovite dehydration melting.*

Within muscovites, many trace elements show two distinct elemental groupings (Figure 5.9) for 1.AS and 1(B)MP: Pb, Cs, Mg, Cr, V, and Sc. The most notable trend is for V and Cr, both of which are absent from the pegmatite, but average 292 ppm (V) and 149 ppm (Cr) in the schist. With 1.AS and 1(B)MP derived from the same physical hand specimen (Figure 4.25), this systematic depletion in V and Cr, as well as other trace elements, must be concerned with the melting process. Similarly, biotite also shows distinct trace element contents for Nb, V and Cr (Figures 5.10 & 5.11). The trend for V and Cr is the same; with biotite in the pegmatite attaining negligible Cr and V, whilst biotite in the schist averages 369 ppm (V) and 221 ppm (Cr) (Table 5.17).

The depletion of V and Cr in the pegmatite may be indicative of a lack of mica melting. This is because micas are the principal hosts of V and Cr in this case study (Tables 5.15, 5.16 & 5.17). However, later sections discuss the necessity for some mica melting, and plagioclase (Rb/Sr v Ba) data is indicative of H₂O-present muscovite dehydration melting (Figure 6.1 & Briggs and Cottle

(2018)). Therefore, it is important to consider other means for this observed depletion in the pegmatite. V and Cr are both transition metals, and consequently their valence state controls their substitution into solid/melt (White, 2018). V has four possible valence states, and Cr has five. If the oxidation state during anatexis did not facilitate V and Cr to attain valence states that allow them to substitute into the octahedral site of micas (+2/+3), then this may explain their depletion. In short, if the pegmatite formed under more oxidising conditions than the schist, these transition metals may be preferentially hosted in accessory phases (such as magnetite, ilmenite etc) (White, 2018). This is corroborated by concentrations of V and Cr being strongly dependent on magnetite and ilmenite (Nehring et al., 2010).

6.1.2 Constraining Temperature

In this section, we attempt to constrain temperature using an empirical geothermometer. We then discuss the limitations and compare with existing thermometry in the region, to provide a complete view on formation temperature. As outlined in Section 1.2, there are three principal anatectic processes that produce granitic melts within the continental crust (Sallet et al., 2023; Weinberg & Hasalová, 2015): 1) Fluid-absent biotite and amphibole dehydration melting, which occurs between 850 and 900 °C (Michaud et al., 2021; Patiño Douce & Beard, 1995; Peterson et al., 1991; Pickering & Johnston, 1998; Sallet et al., 2015; Sallet et al., 2023; Skjerlie & Johnston, 1993, 1996; Thompson, 1982; Vielzeuf & Holloway, 1988), 2) Fluid-absent muscovite dehydration melting, between 650-700°C (Anenburg & Katzir, 2014; Brearley & Rubie, 1990; Castro et al., 2000; Dyck et al., 2020; Gardien et al., 1995; Michaud et al., 2021; Patiño Douce & Harris, 1998; Sallet et al., 2023; Storre, 1972), and 3) fluid-present partial melting, between 600-700°C, within which there are many possibilities (Acosta-Vigil et al., 2006; Beard & Lofgren, 1991; Beard et al., 1994; Carroll & Wyllie, 1990; Gardien et al., 2000; Genier et al., 2008; Holtz & Johannes, 1991; Sallet et al., 2015; Sallet et al., 2023; Sawyer, 2010; Weinberg & Hasalová, 2015). One key distinction between these anatectic processes is the temperature range, therefore making constraining temperature key in identifying melting processes.

Melting temperature also informs on more specific melting reactions, and has significant implications for melting of key phases concerned with melt trace element enrichment (Koopmans et al., 2023; Kunz et al., 2022). Kunz et al. (2022) highlight the significance of higher temperatures to facilitate biotite melting reactions that release certain critical metals into the melt: Li, Be, Sn, Cs and W. Alternatively, Kunz et al. (2022) find that Cs and Be concentrations “start to decrease” upon crossing the muscovite solidus, indicating release into melt. Other research also evidences the significant implications biotite breakdown can have on partial melt compositions. For example, Conrad et al. (1988) communicate how incongruent melting reactions involving the consumption of biotite “greatly influence” near-solidus partial melt compositions. Within this near-solidus melting, biotite, plagioclase, and quartz break down to produce compositions with variable amphibole, garnet, and

pyroxene depending upon temperature and aH₂O (Conrad et al., 1988). As such, constraining metamorphic/melt temperature is vital in understanding processes that might affect metal enrichment. In this section, the application of a Ti-in-biotite geothermometer is used to provide insight into temperatures.

Titanium-in-biotite thermometer

Biotite compositions have been shown to change systematically with temperature. Patiño Douce and Johnston (1991) observe a strong positive correlation between increasing temperature and enrichment of TiO₂, F, and Mg/Fe ratio within biotites (see Fig. 9 in Patiño Douce and Johnston (1991)). This was shown experimentally for melting of biotite-bearing assemblages. TiO₂ content can be used to distinguish magmatic biotite from hydrothermal biotite. Magmatic biotite commonly forms at higher temperature and contains more TiO₂ (Feng et al., 2021; Henry et al., 2005; Patiño Douce & Harris, 1998; Stussi & Cuney, 1996). Henry and Guidotti (2002) investigated the Ti contents of biotite in pelitic schists. Their biotite dataset shows an inverse linear relationship between Ti and Mg contents and facilitates the calculation of a Ti saturation surface for biotite in relation to temperature and Mg. Henry et al. (2005) build on the work of Henry and Guidotti (2002) and consider the geothermometry relative to biotite Ti-saturation more generally. Henry et al. (2005) calibrate the relationship between Ti, temperature, and Mg/(Mg+Fe) empirically using a data set for biotites (n=529). Henry et al. (2005) also identify compositional and textural indications of biotite disequilibrium and localised equilibrium, such as oriented sagenitic rutile in biotite with minor degrees of chloritization, the development of differing colours within biotite due to retrogression, and intergranular and intragranular compositional variance. These factors are generally assumed to have negligible effect in biotite of this study as they are not observed, although limitations to the applicability of this method are outlined later.

The empirical geothermometer proposed by Henry et al (2005) is concerned with the Ti content of biotites within “graphitic, peraluminous metapelites that contain ilmenite or rutile and have equilibrated at roughly 4-6kbar” (Henry et al., 2005). This thermometer is applicable to 1.AS, 1.AS.H, and 1(B)MP because these samples have the relevant phase assemblage and inferred pressure of formation (Wallace, 1974). The geothermometer considers the relationship between Ti-abundance, temperature and Mg/(Mg+Fe), and is denoted by the following expression;

Equation 6.1: $T = \{[\ln(Ti) - a - c(X_{Mg})^3]/b\}^{0.333}$, (T=°C, Ti = a.p.f.u, X_{Mg} = Mg/(Mg+Fe), a = -2.3594, b=4.6482 x 10⁻⁹ and c=-1.7283 (Henry et al., 2005)). This expression is calibrated for the following ranges: X_{Mg}=0.275 – 1.000, Ti = 0.04 – 0.60 a.p.f.u, and T = 480 – 800°C. The geothermometric expression of Henry et al. (2005) (Equation 6.1), was applied to all individual biotite samples in this study. Henry et al., (2005) provide an estimated uncertainty of approximately ±24°C at 480-600°C.

Table 6.2: Summary of calculated biotite temperatures for each rock sample.

	Temperature (°C)			
	Maximum	Minimum	Mean	Standard Deviation
1.AS (n=32)	636	483	548	36
1(B)MP (n=24)	614	539	580	19
1.AS.H (n=38)	646	494	579	34

Table 6.3: Relevant data and parameters and thermometry calculations for biotite temperatures after Henry et al., (2005). NB: $a=-2.3594$, $b=4.6482 \times 10^{-9}$, $c=-1.7283$ and data has been converted to 3 decimal places. Suffix "C" indicates grain core, suffix "R" indicates grain rim, suffix "(M)" indicates matrix grain.

Sample	Analysis name	Ti (apfu)	ln(Ti)	Mg/(Mg+Fe)	Calculated Temperature °C
1.AS	1.AS L167 C	0.298	-1.210	0.339	636
1.AS	1.AS L200 'C'	0.187	-1.679	0.341	541
1.AS	1.AS L205 C	0.221	-1.508	0.342	579
1.AS	1.AS L216 C	0.271	-1.305	0.317	616
1.AS	1.AS L227 C	0.164	-1.811	0.348	508
1.AS	1.AS L228 C	0.177	-1.730	0.351	530
1.AS	1.AS L167 R	0.200	-1.610	0.341	557
1.AS	1.AS L189 R1	0.199	-1.617	0.347	556
1.AS	1.AS L216 R	0.186	-1.684	0.340	539
1.AS	1.AS L228 R	0.227	-1.483	0.312	581
1.AS	1.AS L6(M)	0.166	-1.797	0.347	512
1.AS	1.AS L12(M)	0.176	-1.735	0.361	530
1.AS	1.AS L23 (M)	0.234	-1.452	0.348	592
1.AS	1.AS L29 (M)	0.150	-1.897	0.367	487
1.AS	1.AS L64 (M)	0.194	-1.642	0.344	550
1.AS	1.AS L137 (M) Bt	0.181	-1.707	0.359	537
1.AS	1.AS L144 (M) Bt1	0.151	-1.892	0.372	490
1.AS	1.AS L185 (M)	0.172	-1.763	0.357	523
1.AS	1.AS L198 (M)	0.211	-1.554	0.300	565
1.AS	1.AS L203 (M)	0.164	-1.808	0.373	514
1.AS	1.AS L204 (M)	0.238	-1.435	0.346	595
1.AS	1.AS L215 (M)	0.188	-1.672	0.343	543
1.AS	1.AS L116 Bt2	0.221	-1.508	0.365	582
1.AS	1.AS L116 Bt3	0.214	-1.542	0.351	573
1.AS	1.AS L145 Bt1	0.202	-1.601	0.358	561
1.AS	1.AS L153 Bt2	0.206	-1.581	0.334	563
1.AS	1.AS L160 Bt	0.233	-1.455	0.344	590
1.AS	1.AS L166 Bt	0.145	-1.934	0.398	483
1.AS	1.AS L184	0.174	-1.749	0.372	529
1.AS	1.AS L214	0.180	-1.717	0.355	534
1.AS	1.AS L221 Bt	0.168	-1.784	0.344	515
1.AS	1.AS L229 Bt	0.175	-1.743	0.332	523
1(B)MP	1(B)MP L52 C5	0.241	-1.423	0.301	592
1(B)MP	1(B)MP L53 C	0.231	-1.466	0.304	584
1(B)MP	1(B)MP L79 C1	0.190	-1.659	0.290	539
1(B)MP	1(B)MP L81 C1	0.218	-1.522	0.289	571
1(B)MP	1(B)MP L129C	0.226	-1.488	0.293	578
1(B)MP	1(B)MP L129 C2	0.229	-1.476	0.317	583
1(B)MP	1(B)MP L52 R1	0.251	-1.381	0.277	598
1(B)MP	1(B)MP L52 R6	0.212	-1.551	0.310	566
1(B)MP	1(B)MP L53 R2	0.253	-1.373	0.282	600
1(B)MP	1(B)MP L53 R3	0.205	-1.584	0.316	560
1(B)MP	1(B)MP L54 R1	0.257	-1.360	0.297	604
1(B)MP	1(B)MP L54 R2	0.255	-1.366	0.299	603

1(B)MP	1(B)MP L79 R1	0.202	-1.600	0.295	554
1(B)MP	1(B)MP L79 R5	0.208	-1.569	0.296	561
1(B)MP	1(B)MP L81 R1	0.246	-1.404	0.281	594
1(B)MP	1(B)MP L83 R3	0.223	-1.503	0.281	574
1(B)MP	1(B)MP L129 R	0.233	-1.457	0.290	584
1(B)MP	1(B)MP L84(M)	0.219	-1.517	0.337	577
1(B)MP	1(B)MP L87(M)	0.271	-1.306	0.295	614
1(B)MP	1(B)MP L86(M)	0.213	-1.548	0.297	565
1(B)MP	1(B)MP L88(M)	0.196	-1.632	0.327	550
1(B)MP	1(B)MP L89(M)	0.238	-1.436	0.282	588
1(B)MP	1(B)MP L93(M)	0.241	-1.424	0.287	591
1(B)MP	1(B)MP L94(M)	0.228	-1.478	0.321	583
1.AS.H	1.AS.H L2 'C'	0.165	-1.800	0.456	535
1.AS.H	1.AS.H L20 C	0.146	-1.923	0.442	498
1.AS.H	1.AS.H L20 C2	0.168	-1.783	0.451	538
1.AS.H	1.AS.H L24 C	0.197	-1.626	0.444	572
1.AS.H	1.AS.H L25 C	0.193	-1.647	0.443	567
1.AS.H	1.AS.H L28 C	0.221	-1.510	0.452	597
1.AS.H	1.AS.H L32 C	0.233	-1.456	0.430	603
1.AS.H	1.AS.H L51 C	0.226	-1.487	0.437	599
1.AS.H	1.AS.H L52 C	0.221	-1.509	0.405	588
1.AS.H	1.AS.H L54 C Bt	0.219	-1.518	0.429	591
1.AS.H	1.AS.H L79 C	0.264	-1.333	0.383	619
1.AS.H	1.AS.H L107 C	0.229	-1.473	0.405	596
1.AS.H	1.AS.H L108 C	0.195	-1.635	0.406	562
1.AS.H	1.AS.H L110 C1	0.232	-1.460	0.367	592
1.AS.H	1.AS.H L24 R	0.145	-1.931	0.434	493
1.AS.H	1.AS.H L25 R	0.190	-1.658	0.447	565
1.AS.H	1.AS.H L28 R	0.197	-1.623	0.440	571
1.AS.H	1.AS.H L32 R Bt	0.249	-1.390	0.445	619
1.AS.H	1.AS.H L32 R2 Bt	0.231	-1.464	0.418	600
1.AS.H	1.AS.H L51 R	0.177	-1.731	0.440	547
1.AS.H	1.AS.H L52 R	0.218	-1.524	0.417	588
1.AS.H	1.AS.H L53 R Bt	0.253	-1.373	0.415	616
1.AS.H	1.AS.H L54 R Bt	0.203	-1.596	0.419	573
1.AS.H	1.AS.H L79 R	0.302	-1.198	0.408	646
1.AS.H	1.AS.H L107 R Bt	0.203	-1.597	0.361	563
1.AS.H	1.AS.H L108 R	0.236	-1.443	0.393	600
1.AS.H	1.AS.H L110 R	0.228	-1.479	0.369	589
1.AS.H	1.AS.H L21 (M)	0.182	-1.704	0.448	555
1.AS.H	1.AS.H L22 (M)	0.205	-1.583	0.448	582
1.AS.H	1.AS.H L43 (M)	0.143	-1.945	0.463	498
1.AS.H	1.AS.H L70 (M)	0.169	-1.776	0.413	530
1.AS.H	1.AS.H L80 (M)	0.251	-1.380	0.404	613
1.AS.H	1.AS.H L96 (M)	0.244	-1.411	0.408	608
1.AS.H	1.AS.H L96 (M)	0.224	-1.497	0.425	595
1.AS.H	1.AS.H L96 (M)	0.227	-1.482	0.424	597
1.AS.H	1.AS.H L96 (M)	0.253	-1.375	0.438	620
1.AS.H	1.AS.H L26 Bt	0.224	-1.497	0.426	595
1.AS.H	1.AS.H L26 Bt2	0.219	-1.518	0.453	596
1.AS.H	1.AS.H L50 Bt	0.202	-1.597	0.446	578

Figure 6.2 and Table 6.3 show the calculated temperatures for biotite in 1.AS, 1(B)MP and 1.AS.H. Calculated temperatures average 548°C, 580°C, and 579°C in 1.AS, 1(B)MP and 1.AS.H, with standard deviation values of 36°C, 19°C and 34°C respectively (Table 6.2). Temperatures are within the expected range for the garnet-biotite schists, and generally align with other temperature estimates

(Figure 6.3 & Beyssac et al. (2016)). 1.AS ranges from 483°C to 635°C, covering the whole temperature range from chlorite zone greenschists, up to the upper end of garnet oligoclase amphibolites of Beyssac et al. (2016). However, the sample 1(B)MP returns temperatures lower than those reported by other studies on the Mataketake Pegmatites (620-700°C, (Beyssac et al., 2016; Briggs & Cottle, 2018; Wallace, 1974)). We expand on these observations in the subsection *Comparison with existing thermometry*. The temperatures for 1(B)MP cover a more confined range relative to the two schist samples (Table 6.2) and are constrained to 539°C to 614°C, consistent with formation via partial melting of the Alpine Schist.

Analyses were separated into cores, rims and matrix, denoted by “C”, “R”, and “(M)” respectively (see Chapter 3 for identification processes for these intragrain locations). Grains that did not fit within the grouping criteria for these subcategories fall into “Other” (Figure 6.2). There is no clear relationship between calculated temperatures and intragrain position of analyses (Figure 6.2).

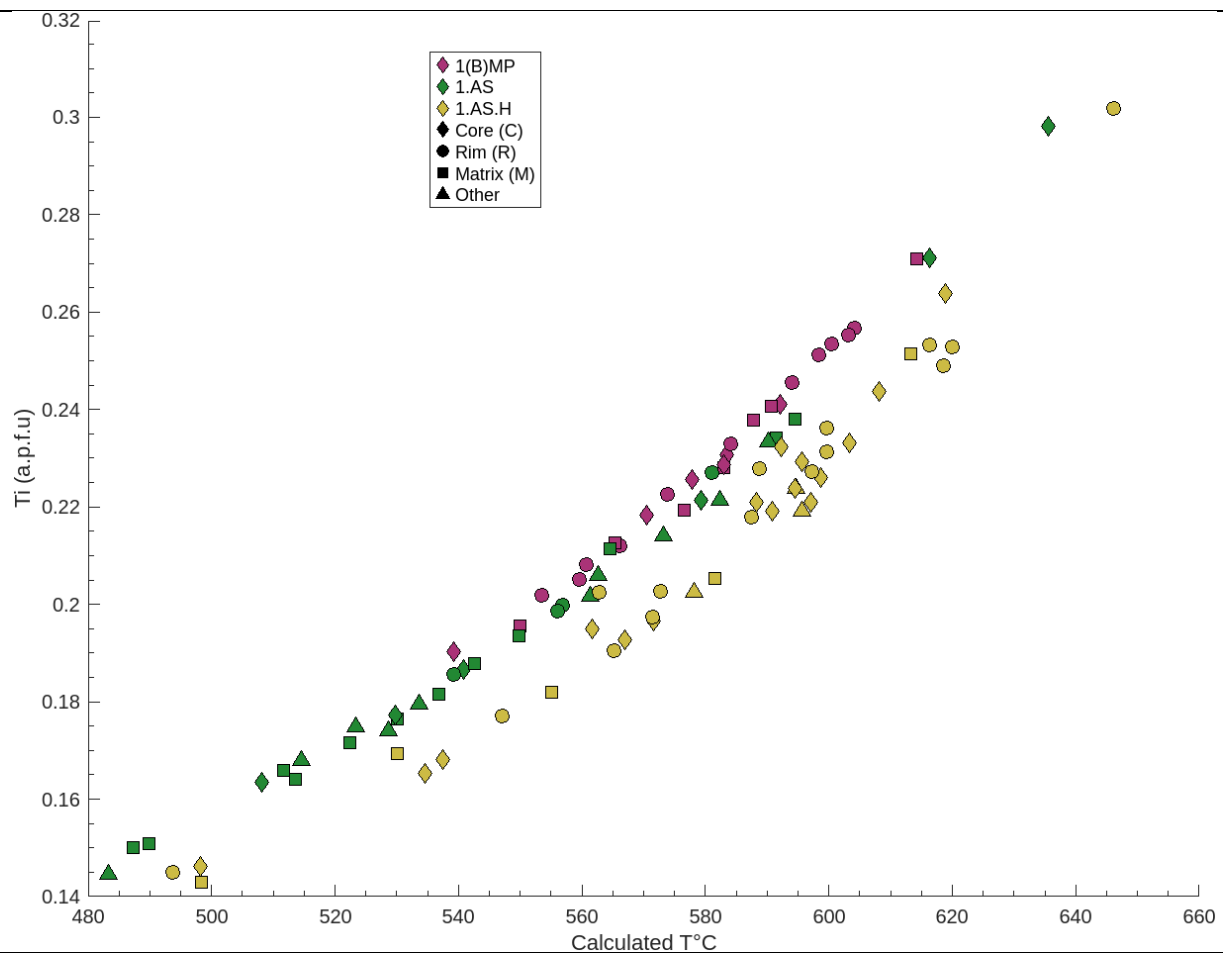


Figure 6.2: Calculated biotite crystallisation $T^{\circ}\text{C}$ after Henry et al (2005), against Ti (a.p.f.u). 1(B)MP is limited to a more confined temperature range than 1.AS and 1.AS.H, reflecting that these biotite grains precipitated under more homogenous conditions following anatexis. There is no apparent trend between core, rim and Matrix grains, indicating alteration has not affected the grains. Typical uncertainties on temperature are approximately $\pm 24^{\circ}\text{C}$. See Figure 6.3 for comparison relative to existing thermometry.

Limitations

The limitations to the application of this geothermometric modelling are as follows. Firstly, the X_{Mg} values for the biotites are on the lower limit of the calibrated range (0.275 – 1.000, Henry et al. 2005), with some data for 1(B)MP falling below the lower limit. These datapoints were excluded to mitigate unnecessary uncertainty. The average X_{Mg} for 1.AS, 1(B)MP, and 1.AS.H were 0.348, 0.299, and 0.426 respectively. All Ti a.p.f.u values fall within the calibrated range of 0.04 – 0.60. The minimum a.p.f.u Ti value was 0.055, and the maximum was 0.310 for analysed biotite samples. The accuracy of the Ti-in-biotite thermometer is principally derived from the accuracy of the petrogenetic grid of Spear et al. (1999). This petrogenetic grid plots isogradic reactions which were used to determine metamorphic pressures and temperatures to formulate the geothermometric expression of Henry et al. (2005). Hence, this model assumes these petrogenetic grids are accurate for the samples studied.

The model of Henry et al. (2005) is equilibrated at roughly 4-6kbar. The metamorphic regime within the South Island varies, which may limit applicability of this empirical geothermometer. Within the Franz Josef-Fox area, metamorphic conditions peaked between 9.2-10 kbar (Grapes & Watanabe, 1992). However, in the Mataketake Range, pressure is constrained to 4.7-7.3 kbar within K-feldspar zone schist (Wallace, 1974). Grapes (1995) confine pressures to >4kbar for the formation of peraluminous granitic melt in the Alpine Schist. Therefore, pressure is assumed to comply with the samples used by Henry et al. (2005) to formulate the empirical geothermometer, however, if the formation pressure deviated from this, this may introduce uncertainty, particularly for 1.AS.H, which originated in the Franz Josef-Fox area.

All geothermometric models assume equilibrium. However, there are significant observed textures that point to post-emplacement deformation for the Mataketake Pegmatite (see Section 4). This is important as biotite can often be altered, replaced, undergo retrogressive cation exchange or to be reequilibrated due to thermal overprinting, means that its application as a geothermometer is strictly reliant on chemical equilibrium. Biotite compositions are prone to change, particularly in the presence of a late fluid-phase, and Ti contents can fluctuate due to disequilibrium and/or localised equilibrium (Henry et al., 2005). Multiple synmetamorphic recrystallisation and deformation events are also documented in other structural and microtextural studies on the region (Andrews et al., 1974; Cooper, 1974; Grapes & Otsuki, 1983; Grindley, 1963; Holm et al., 1989; Lillie et al., 1957; Lillie & Mason, 1955; Pitcairn, 2004; Wallace, 1974). It is therefore possible that the calculated temperatures using the empirical geothermometer of Henry et al (2005) (Table 6.3) reflect the most recent period of deformation, and that the extent to which this reequilibration has affected biotite compositions provides the reason for the observed temperature range. However, we do not observe the alteration or retrogressive textures noted by (Henry et al., 2005). Additionally, the absence of systematic disparities

between grain cores and rims (Figure 6.2), is conducive with a lack of reequilibration. Therefore, we do not expect biotite alteration/replacement to have significantly altered the calculated temperatures, and we conclude that, despite the rock samples having been exposed to multiple deformation events and extensive fluid-rock interactions, the application of Ti-in-biotite is valid.

The geothermometric expression of Henry et al., (2005) was studied for graphitic, peraluminous metapelites, with a Ti-saturating phase. There are two reasons why this might give rise to inaccuracy. Firstly, neither 1.AS and 1(B)MP contain carbonaceous material, whereas 1.AS.H does. 1.AS.H temperatures range from 494-646°C, which is comparable to the temperatures ranging from biotite-zone to K-feldspar-zone using RSCM thermometry (Beyssac et al., 2016). Henry et al. (2005) find that where graphite is absent, the calculated Ti-in-biotite temperatures are commonly lower. This is because the H₂O contents of metamorphic fluids are often greater than their graphite-bearing counterparts. As Ti can substitute for OH in the biotite lattice, increased H₂O in metamorphic fluids increases the availability for H₂O to occupy the hydroxyl site, making Ti-substitution here more difficult. In short, increased H₂O may reduce the extent to which the deprotonation exchange reaction $R^{2+} + 2(OH)^{1-} = Ti^{4+} + 2O^{2-}$ can incorporate Ti in biotite (Henry et al., 2005). As such, Ti abundance in biotite, and inferred Ti-in-biotite temperatures may be lower in non-graphitic samples.

Secondly, for peraluminous metapelites without a Ti-saturating mineral, there can be moderate to large temperature underestimates (Henry et al. (2005) with a magnitude ~60°C (Waters & Whales, 1984) to ~80°C (Patiño Douce & Harris, 1998)). This does not apply to this case study, as all sample contain a Ti-saturating mineral. However, in scenarios where Ti-saturating minerals are present, but graphite is absent, average temperature estimates are often “reasonable”, but may be “erratic” (referring to a greater spread in variance/standard deviation values) (Henry et al., 2005). For example, in the Ballachulish contact metamorphic aureole, temperatures are underestimated by only 9°C on average, but the standard deviation is large $\pm 50^\circ\text{C}$ ((Henry et al., 2005); based on data from (Pattison, 1985, 1987, 1989, 1991; Pattison & Harte, 1991; Pattison et al., 2002). Ilmenite, rutile and titanite (Ti-bearing phases) are all present in the 3 rock samples studied in this thesis, therefore it is assumed the average temperatures are “reasonable”. Yet, the absence of graphite may contribute to a greater variance about this “reasonable” average.

In this section, we have isolated formation temperatures of biotite within the three rock samples using a geothermometer, which functions through the correlation of Ti-in-biotite contents and temperature. Biotite temperatures spread from 483 to 646°C, with the pegmatite averaging higher temperatures (580°C; 1(B)MP) than its adjacent schist (548°C; 1.AS). Notably, the pegmatite attains a more confined range of temperatures (Table 6.2, Figure 6.2). This possibly communicates crystallisation following anatexis, where closure temperature would be more consistent than the array of temperatures a regionally metamorphosed specimen would be exposed to. We analysed biotite rims,

cores and matrix grains (Figure 6.2), but we did not notice any trend between intragrain locations and temperature. After discussing the possible limitations within the geothermometer and our application of the thermometer, we tentatively accept the accuracy of our calculated temperatures. However, to strengthen this, we now consider our temperatures in relation to existing thermometry.

Comparison with existing thermometry

We now consider these results in relation to existing thermometry on the region (Figure 6.3). This study calculates Ti-in-biotite temperatures between 539-614°C (average of 580°C) for the Mataketake Pegmatites. This range is just lower than the proposed range of 620-680°C (Wallace, 1974). The highest temperature of 614°C (this study) is lower than the inferred upper temperature limit of Alpine Schist from Beyssac et al., (2016), where extrapolation of datasets implies maximum temperatures may have reached 700°C. Discrepancies between temperatures calculated in this study and those of existing independent temperature estimates ((Figure 6.3) e.g., (Beyssac et al., 2016; Wallace, 1974)) may be due to the model proposed by Henry et al (2005), issues with independent temperature estimate(s), extrapolation of the empirical geothermometer outside of given ranges, disequilibrium, (including localised equilibrium), or changes to biotite post peak T conditions (such as alteration or reequilibration).

The Ti-in-bt temperatures produced using the expression of Henry et al. (2005) can be considered relative to other well-constrained temperature estimates, produced from independent geothermometers/petrogenetic grids. Grapes and Watanabe (1992) use a Fe-Mg exchange thermometer for garnet-biotite, and a garnet-biotite-muscovite-plagioclase geobarometer (see references therein), to derive P-T estimates. In the Franz Josef-Fox area, (which contains 1.AS.H), metamorphic conditions peaked in the region of 600-700°C and 9.2-10kbar (Grapes & Watanabe, 1992). In contrast, Wallace (1974) uses the observed assemblages from petrographic analyses and experimentally calibrated reactions to suggest a P-T range for melting in the Mataketake Range; between ~620-680°C and 4.5-7.2kbar for reactions that involve K-feldspar, which is not present in 1.AS, 1(B)MP and 1.AS.H. These temperatures align with the upper-range of temperatures generated in this study. The presence of K-feldspar in the reactions used to infer temperature constraints on the Mataketake Region by Wallace (1974), may decrease the applicability of Wallace's temperature estimates for this study. However, the inclusion/exclusion of K-feldspar in melting reactions does not significantly affect melting temperatures (Weinberg & Hasalová, 2015). Additionally, Wallace (1974) proposes water-present melting as the production mechanism for the Mataketake Pegmatites. Water-present melting for rocks of felsic-intermediate compositions, are not "particularly" sensitive to compositional variation (see Weinberg and Hasalova (2015) and references therein). Therefore, we consider the temperature estimates of Wallace (1974) to remain relevant to this study.



Figure 6.3 Recorded and proposed temperatures in literature for rock samples within the Mataketake Range and surrounding regions. From left to right: **1)** This Study - Alpine Schist, (483-636°C), temperatures obtained from Ti-in-biotite geothermometer, **2)** This Study - Alpine Schist (Hare-Mare region), (494-646°C) temperatures obtained from Ti-in-biotite geothermometer, **3)** This Study - Mataketake Pegmatites, (539-614°C), temperatures obtained from Ti-in-biotite geothermometer, **4)** Beyssac et al. (2016) - Garnet-Oligoclase zone Alpine Schist (515-640°C; Figure 6.4), temperatures obtained from RSCM thermometry (Section 2.2.1), **5)** Beyssac et al. (2016) - Extrapolation of metamorphic temperatures starting at 640°C in the Southern region of Alpine Fault (Copland, Karangarua, Moeraki, Otoko & Haast (Locations in Figure 6.4), see Figure 10 in Beyssac et al. (2016), temperatures obtained from RSCM thermometry (Section 2.2.1), **6)** Wallace (1974), (625-680°C) - Proposed metamorphic temperatures in Mataketake Range and “similar” conditions to formation of pegmatites, temperatures obtained from experimentally calibrated reactions and petrology, **7)** Grapes and Watanabe (1992) & Grapes (1995), (600-700°C) - Peak metamorphic temperatures for Alpine Schist in the Franz-Josef-Fox area (20-30km northeast of Copland (see Figure 6 in Beyssac et al. (2016)), & **8)** Briggs and Cottle (2018) - Alpine Schist temperatures of “at least 650°C” to facilitate partial melting, no upper bound given.

Beyssac et al. (2016) use Raman spectroscopy on carbonaceous material (RSCM) thermometry to calculate maximum metamorphic temperature. Unlike other thermometers (e.g., chlorite thermometry, Ti-in-biotite, Fe-Mg exchange thermometers (Berman et al., 1995; Beyssac et al., 2016; Beyssac et al., 2002; Bourdelle et al., 2013; Grapes & Watanabe, 1992; Henry & Guidotti, 2002; Henry et al., 2005)), RSCM is not affected by the retrograde path during exhumation, and solely records the highest temperature during metamorphism (Beyssac et al., 2016; Beyssac et al., 2002). This makes it

an appropriate thermometer to use in relation to the Alpine Schist and Mataketake Pegmatite. The Mataketake Range lies between the Haast River to the southwest, and the Moeraki River to the northeast (Figure 6.4). Along the Moeraki River, Beyssac et al. (2016) confine temperatures to 519°C (garnet-biotite-albite zone), 552°C (biotite zone), 578-587°C (garnet oligoclase zone), and upwards of 640°C for the K-feldspar zone, which is proximal to the Alpine Fault. Temperatures of metamorphism near the Haast River are in the range from 487°C (biotite zone), 573-583°C (garnet oligoclase zone), to $\geq 640^\circ\text{C}$ for the K-feldspar zone ((Beyssac et al., 2016) Figure 6.4).

Summarising 6.1.2

This study has generated temperatures between 483°C and 636°C for the Alpine Schist in the Mataketake Region (1.AS). The Mataketake Range is situated between the Haast River and Moeraki River (see Figure 6.4 from Beyssac et al., (2016)). 483°C aligns with the upper end of chlorite-zone temperatures. 636°C lies just below K-feldspar zone temperatures, in the garnet-oligoclase zone. The majority of 1.AS samples align with the biotite zone and the garnet-oligoclase zone of Beyssac et al. (2016). Mineralogically, 1.AS would be described as garnet-oligoclase. Therefore, this study agrees with that of Beyssac et al. (2016), however the temperatures generated in this study do cover a wide temperature range and two metamorphic zones. For Alpine Schist in the Hare-Mare creek, this study calculates temperatures between 494°C and 646°C (1.AS.H). Hare-Mare creek lies on the Waikukupa River, which attains temperatures of 395-555°C for the biotite zone, 530-565°C for the garnet-oligoclase zone, and $\geq 640^\circ\text{C}$ for the K-feldspar zone (Beyssac et al., 2016). We therefore record temperatures that span the biotite zone, through the garnet-oligoclase zone, and creep into the K-feldspar zone of Beyssac et al. (2016). Again, this aligns with the mineralogy within 1.AS.H (a garnet-biotite-oligoclase gneiss (although named Alpine ‘Schist’)). However, the temperatures do span a wide range for a single hand specimen. For the Mataketake Pegmatites, we generate temperatures between 539°C and 614°C, with an average of 580°C. Beyssac et al. (2016) do not measure formation temperatures of the Mataketake Pegmatites. Instead, within the Mataketake Region they attain temperatures $\geq 640^\circ\text{C}$ for K-feldspar zone metamorphic rocks proximal to the Alpine Fault, and 573-587°C for the garnet-oligoclase zone. Therefore, our temperature average aligns with the higher-grade metamorphic facies in the Mataketake Region. Again however, our temperatures do span a range of metamorphic zones identified by Beyssac et al. (2016), with our lowest temperature pegmatites aligning with the biotite zone of Beyssac et al. (2016).

Our research provides new temperature estimates for the Alpine Schist at Hare-Mare and in the Mataketake Region, as well as for the Mataketake Pegmatites. However, we are tentative suggesting the accuracy of these temperatures, due to reasons set out in “Limitations”. We believe the greatest source of uncertainty is the possibility for reequilibration during a more recent deformation period, to have affected biotite compositions. As such, it is important for temperatures to be considered in relation to existing thermometry.

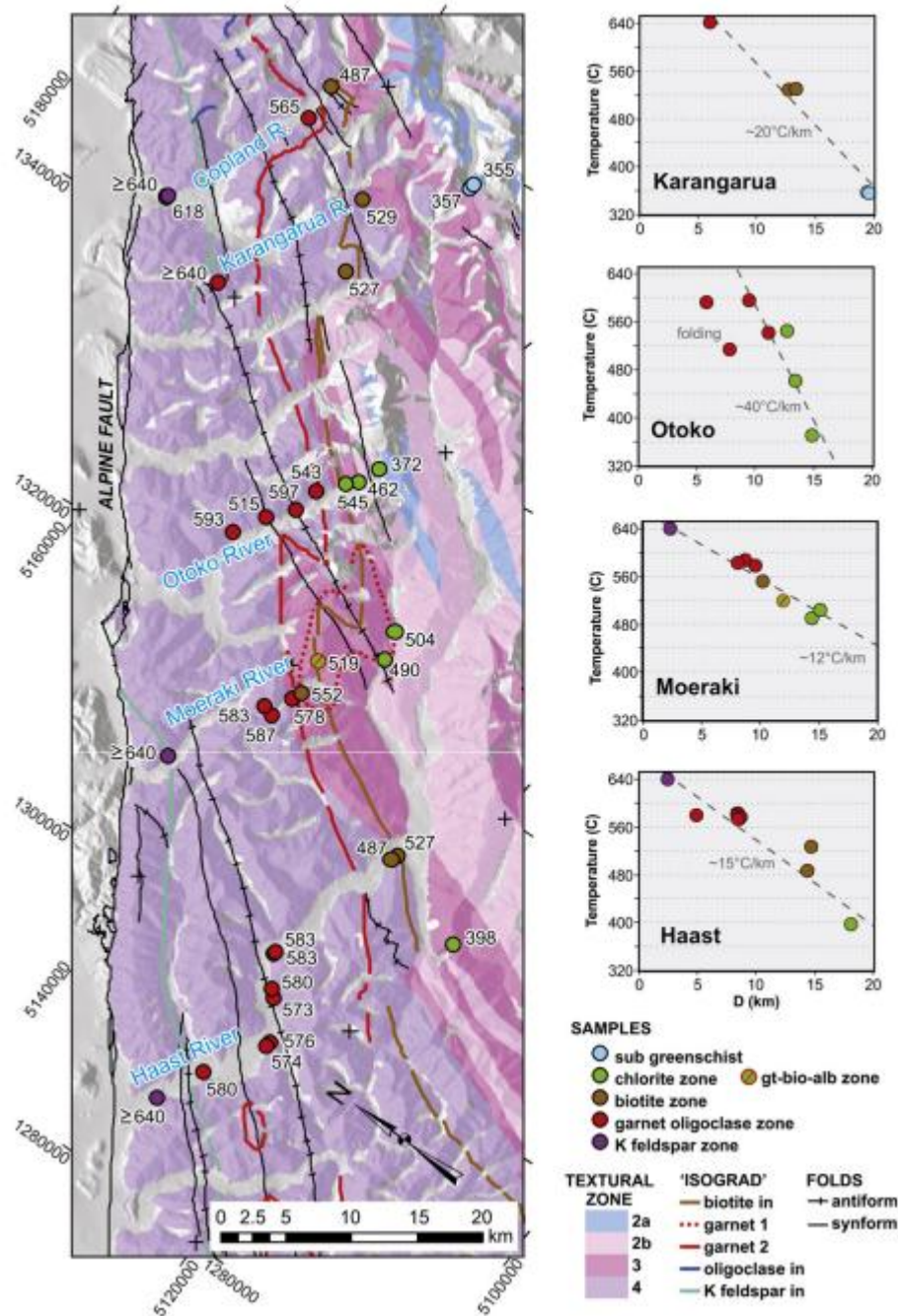


Figure 6.4: Beyssac et al. (2016) constrain metamorphic temperatures along the Alpine Fault. The Mataketake Range is situated between the Haast River and the Moeraki River.

We propose our temperature estimates manifest a lower-bound for possible formation temperatures, as if a more-recent deformation event has affected biotite compositions, then it will have reequilibrated the biotites at a lower temperature. Therefore, we use our calculated temperatures, as well as other thermometry (Beyssac et al., 2016; Grapes & Watanabe, 1992; Wallace, 1974) to propose a temperature range of 539°C (This Study) to 700°C (Beyssac et al., 2016), for the formation of the Mataketake Pegmatites. This temperature range is then used to consider melting processes, including the potential for muscovite/biotite melting, to inform on enrichment of metals such as Li. Regarding

pegmatite classification, temperature and petrological (which provides geological context) constraints place this pegmatite within the “Muscovite” class (see Section 1.2 (Černý & Ercit, 2005)).

6.1.3 Melt Processes, Reactions and Composition

In this subsection, we use temperatures, geochemistry, and compositional variation to infer melting processes, reactions, and to calculate melt composition. Bulk rock compositions can provide important insight into possible melting/crystallisation processes, reactions, and chronology of mineralogical precipitation. Normative whole rock compositions are calculated using mineralogical compositions (Laser ICP-MS and SEM-EDS) and mineralogical abundances. Normative An-Ab-Or are then plotted to infer melting processes. The bulk melt composition of the pegmatite is estimated from the thin section using SEM-EDS for major elements and Laser ICP-MS for trace element data, using simple partitioning calculations and basic mass-balance modelling. Elemental modelling in this study considers the four principal phases within the Alpine Schist & Mataketake Pegmatites: Plagioclase (plag), Muscovite (ms), Biotite (bt), and Quartz (qtz). Collectively, these phases comprise 98.1% of 1.AS, and 99.6% of 1(B)MP (Table 5.1). The concentration of each of the elements is known within plagioclase, biotite, and muscovite (from Laser ICP-MS) but not within quartz. However, with the assumption that trace element substitution within the quartz lattice is negligible, the mass-balance equations were simplified so that quartz component is removed. This reduces the number of unknowns in the mass balance modelling in this section. Section 6.1.2 confines temperatures to the range of 539°C (This Study) to 700°C (Beyssac et al., 2016) for the Mataketake Pegmatites. As outlined in Section 1.2 and discussed in 6.1.2, understanding temperature is vital in identifying possible melting reactions. This temperature range of 539-700°C rules out fluid-absent biotite and amphibole dehydration melting, and therefore leaves us with fluid-absent muscovite dehydration melting (650-700°C), or fluid-present partial melting (600-700°C) as possible melting reactions ((Sallet et al., 2023) see Section 6.1.2). As temperature constraints determine melting reactions, it therefore determines which phases can liberate key elements through their breakdown, a vital consideration for metal enrichment. We discuss this more in Section 6.1.4 and 6.2.

Table 6.4 displays melting reactions from literature which either coincide with conditions for the Mataketake Pegmatite, or are reactions previously proposed for the Mataketake Pegmatites. All reactions in Table 6.4 are generally concerned within the identified temperature range of 539-700°C. In this section, we follow the process set out at the start of this section (6.1.3) to eliminate reactions from Table 6.4, to constrain melting reaction(s) that contributed to the formation of the Mataketake Pegmatites. Notably, Briggs and Cottle (2018) suggest four melting reactions for the Mataketake Pegmatite: (1) *quartz + plagioclase (ab) + K-feldspar (or) + H₂O = melt*; 2) *muscovite + plagioclase + quartz + H₂O = melt*; 3) *garnet + biotite + H₂O = garnet + biotite + melt*; 4) *quartz + K-feldspar + plagioclase + H₂O = plagioclase + melt* (see Briggs and Cottle (2018) and references therein). Of these four reactions, the first and the fourth can be discounted immediately within this study, due to

the absence of K-fsp in the Alpine Schists analysed. These two reactions are therefore excluded from Table 6.4. This leaves us with the second and third reactions as feasible choices. They are included in Table 6.4 (reactions No.2&6, and No.8). Within Table 6.4, reactions No.2 and 6 are included as separate reactions, due to the attributed reaction conditions being different.

Table 6.4: Melting reactions from literature which coincide with conditions for the Mataketake Pegmatite.

No.	Melting Reaction	Conditions	Comments	Reference(s)
1	Bt + Qtz + Plag + H ₂ O = melt	680-690°C/6 kbar	Small decrease in bt, but qtz + plag are greatest contributors. Incongruent fluid-present bt breakdown reactions occur at >720°C	(Watkins et al., 2007; Weinberg & Hasalová, 2015)
2	Ms + Plag + Qtz + H ₂ O = melt	~700-900°C/>6kbar	Only different to No.6 due to different conditions attributed to reaction. Patiño Douce and Harris (1998) quantify this as: 9Ms+15Plag+7Qtz+xH ₂ O=melt.	(Fornelli et al., 2002; Patiño Douce & Harris, 1998; Weinberg & Hasalová, 2015)
3	Ms + Sil + Plag + Qtz ± Grt ± Bt + H ₂ O = melt		No sillimanite observed in 1.AS sample, but Alpine Schist has been proven to be heterogenous in nature.	(Johnson et al., 2003; Weinberg & Hasalová, 2015)
4	Plag + Qtz + Bt + H ₂ O = Ttn + melt	Ca.700°C, influx of H ₂ O		(Sawyer, 2010; Weinberg & Hasalová, 2015)
5	Qtz + Plag + Fluid = melt	Excess H ₂ O, low T	this 'wet' solidus reaction would also consume a very small amount of bt and/or ms	(Clemens et al., 2020; Mayne et al., 2020)
6	Ms + Qtz + Plag (Ab) + H ₂ O = melt ± (aluminium silicate)	200MPa, 625°C	Bt stable over entire range of 600-750°C. Reacts to hercynite + melt at high end of T. Normative melt composition at min is Ab ₃₀ Or ₁₅ Ms ₂₀ Qtz ₃₅ . Icenhower & London (1995) state aluminium silicate within their reaction. Briggs & Cottle (2018) propose this as a possible melting reaction for the Mataketake Pegmatites.	(Briggs & Cottle, 2018; Dyck et al., 2020; Icenhower & London, 1995)
7	Ms + Plag + Qtz = Melt + Kfs + Sil + Bt	700-900°C, ≤1GPa	Ms dehydration melting. Patiño Douce and Harris (1998) quantify this as: 22Ms+7Plag+8Qtz=25Melt+5Kfs+5Sil+2Bt	(Dyck et al., 2020; Patiño Douce & Harris, 1998)
8	Gt + Bt + H ₂ O = Gt + Bt + Melt		One of four reactions proposed by Briggs & Cottle. See references therein.	(Briggs & Cottle, 2018)

6.1.3.1 Constraining Melting Reaction(s)

Independent from the thermometry information (Section 6.1.2), the proportion of normative Ab-An-Or can distinguish melt compositions derived from H₂O-present melting and from dehydration melting (Briggs & Cottle, 2018; Holtz & Johannes, 1991; Inger & Harris, 1993; Patiño Douce & Harris, 1998; Pichavant et al., 1992; Weinberg & Hasalová, 2015). As outlined in Chapter 2, at higher aH₂O, melts become depleted in Or, and become enriched in An and Ab (Briggs & Cottle, 2018; Inger & Harris, 1993; Weinberg & Hasalová, 2015). This is because the melting reaction Quartz + Plagioclase + H₂O, is more dominant than muscovite-melting reactions when fluid is present, due to the quartz+plagioclase solidus being more intensely depressed than the muscovite solidus (Inger & Harris, 1993; Patiño Douce & Harris, 1998; Sallet et al., 2018; Sallet et al., 2023; Weinberg & Hasalová, 2015). Conversely, at decreased water activities, Ebadi and Johannes (1991) observe a significant increase in Or:Ab ratios within minimum-melts of granitic compositions. Calculated normative whole-rock Ab-An-Or data from this study show a progression toward more albitic whole rock compositions in the pegmatite relative to the schist (Figure 6.5). This depletion in Or points to a fluid-present melting scenario, and aligns with existing data from Briggs and Cottle (2018). Plagioclase compositions of this study all have orthoclase contents <0.01 (Figure 5.1). However, there is a notable progression toward more Ab-rich compositions from the Alpine Schist (1.AS & 1.AS.H) to the pegmatite 1(B)MP (Figure 6.5). This suggests fluid-present melting as the mechanism for pegmatite production. Furthermore, as previously discussed (Section 6.1.1.2), whole-rock compositions of Ba vs Rb/Sr indicate fluid-present muscovite dehydration melting (Figure 6.1).

This aligns with previous conclusions of Briggs and Cottle (2018), who propose fluid-present melting as the “dominant” mechanism for the Mataketake Pegmatite. However, they also tentatively indicate that fluid-absent dehydration melting may have contributed to older melts based on older samples within their study trending toward Or-rich compositions (Figure 6.5). There is also their sample MR13-29, which appears as an outlier in their data, with a high Or:Ab ratio, and negligible An component.

Dyck et al. (2020) communicate how granitic melts in orogenic hinterlands are initially produced via muscovite dehydration melting. In fluid-absent scenarios, the dominant reaction is muscovite + quartz = K-feldspar + sillimanite + monzogranitic melts (Reaction 7, Table 6.4). Conversely, in settings where water-vapour is present in excess, muscovite primarily breaks-down to produce sillimanite + melt (Dyck et al., 2020). K-feldspar is only generated due to melt crystallisation. As such, the lack of K-feldspar in pegmatites of this study is consistent with fluid-present melting of the Alpine Schist.

To summarise thus far, major and trace element data show distinct compositions of plagioclase, muscovite and biotite between the schist and pegmatite, indicating the melt origins of the latter (6.1.1). The variation in mineralogical abundances between protolith and the pegmatite implies H₂O-

fluxed muscovite melting at low temperature (6.1.1.1). This is corroborated by calculated whole-rock trace element data for Ba, Rb and Sr (6.1.1.2). The observed depletion in Ba, whilst Rb/Sr remains fairly consistent, aligns with existing data of Briggs and Cottle (2018), and evidences H₂O-present muscovite dehydration melting as the dominant melting reaction (Figure 6.1). Applying the Ti-in-biotite empirical geothermometer of Henry et al. (2005) returns biotite closure temperatures between 483°C and 636°C for the analysed samples. The pegmatite attains a confined temperature range of 539-614°C (average of 580°C). These temperatures fall at the lower end of melting reactions (Table 6.4), aligning with the indicated low-temperature origins of the pegmatite. Considering our calculated temperatures in relation to existing thermometry on the region (Briggs & Cottle, 2018; Wallace, 1974), allows for a viewpoint based on more evidence. We propose a temperature range of 539°C (This Study) to 700°C (Beyssac et al., 2016) for the formation of the Mataketake Pegmatites. This relatively low temperature is suggestive of fluid-present melting and enables us to remove melting reactions that do not align with this temperature range. Calculated normative whole-rock Ab-An-Or abundances in the schist and pegmatite indicate a fluid-present melting scenario (Figure 6.5). To synthesise, evidence so far points to a low-temperature, fluid-present muscovite dehydration melting scenario (Reactions 2 & 6, Table 6.1).

Consequently, of the four melting reactions proposed by Briggs and Cottle (2018), data from this study points to the second (Reaction No.6, Table 6.4). This differs from reaction No.2 (Table 6.4) by temperature. To further isolate possible melting reaction(s) within Table 6.4 and examine our suggestion of fluid-present muscovite dehydration melting, the sections below will estimate the phase proportions involved in the melting reaction inferred to produce 1(B)MP from 1.AS, using first the major elements (K, Fe and Mg (KFM) section 6.1.3.2), then select trace elements, before looking at Lithium specifically.

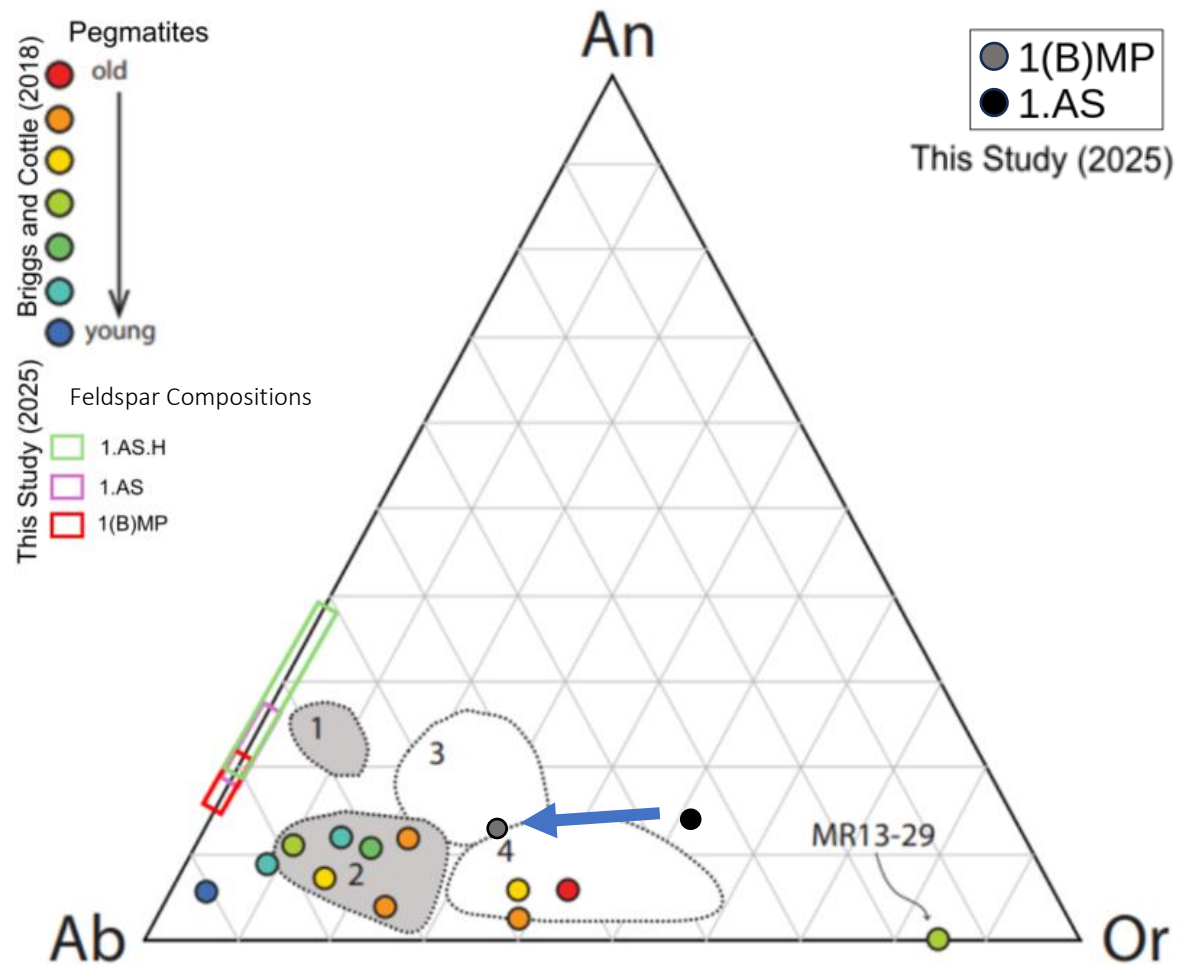


Figure 6.5: Taken from Briggs and Cottle (2018), displaying their normative An-Ab-Or data (whole-rock) for a suite of Mataketake Pegmatites. Data from this study is added; calculated whole-rock normative compositions show a transposition from 1.AS to 1(B)MP toward albitic whole-rock compositions. This change in composition is highlighted by the blue arrow, which also illustrates the general trend for data from this study and (Briggs & Cottle, 2018). The boxes represent data from feldspars of this study (not whole-rock data). Green = Alpine Schist Hare Mare (1.AS.H), Purple = Alpine Schist, Mataketake Region, Red = Mataketake Pegmatite. This data is indicative of fluid-present melting. Regions 1, 2, 3 and 4 represent “melt compositions for dehydration melting reactions (white fields) and water-present melting reactions (gray fields): (1) H₂O-saturated melting of dacite/graywacke (Conrad et al., 1988), (2) H₂O-present melting of mica schist (Patiño Douce & Harris, 1998) (3) H₂O-understaurated melting of dacite/graywacke (Conrad et al., 1988), (4) dehydration melting of tonalite (Patiño Douce, 2005)” (directly quoted from Briggs and Cottle (2018))

6.1.3.2 Geochemical Insights into processes

Firstly, we consider insights from major element data (K, Fe and Mg), before attempting to constrain melt compositions, and reactions using trace element data. We then look at Li, before discussing the limitations with applying equilibrium melting models. Finally, we summarise melting reactions and processes (Section 6.1.4), considering all sections of this discussion.

K₂O, FeO, and MgO (KFM) System

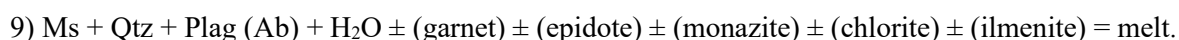
Like the leucogranites studied by Scaillet and Pichavant (2024), biotite and muscovite are the dominant potassium-bearing and ferromagnesian minerals in the pegmatite and schist. This suggests these phases were vital during the formation process (Scaillet & Pichavant, 2024). With plagioclases of this study containing no potassic component, the micas are therefore the only phases that can liberate K, Fe and Mg (KFM) into the melting fraction. Consequently, the extent of mica melting dictates the KFM composition of the produced melt. This allows us to constrain melting scenarios that liberate appropriate quantities of KFM. The average mica compositions in 1.AS and 1(B)MP are listed in Table 5.14).

To precipitate a pegmatite with 19.4% muscovite and 7.6% biotite and compositions as summarised in Table 5.1, there must be at least 2.7wt% K₂O, 1.97wt% FeO and 0.84 wt% MgO contained in the melt (calculated using average mica compositions in the pegmatite (1(B)MP)). If KFM are only sourced from micas, of composition identical to the average 1.AS mica composition, the following scenarios would satisfy the system (Table 6.5). Note how the iron and magnesium components of the system necessitate biotite melting, as without it, 89% of the melting fraction must be comprised of muscovite. Such a high quantity of muscovite in the liquid fraction is not feasible and would result in a melt with 10.14wt% K₂O, which is over 3 times the melt abundance K₂O required to precipitate the Mataketake Pegmatite. A melt of this composition would precipitate a pegmatite dominated by aluminosilicates and would not attain the high quantities of quartz and plagioclase observed (see Section 6.1.1). Alternatively, the system can be satisfied with 28% biotite, and 0 muscovite in the melting fraction (Scenario 3). All scenarios, apart from No.1, demand ~25% mica within the liquid fraction, providing a good idea of the extent to which mica has contributed to the melt. This aligns with interpretations based on compositional variation (modal abundances), where a lesser proportion of mica has contributed to the melt than plagioclase.

The apparent requirement for a biotite melting fraction is disparate from our suggestion of fluid-present muscovite dehydration melting. Reactions No.1, 4 & 8 (Table 6.4) all contain biotite. However, these reactions occur at the upper limit (~700°C) of the constrained temperature in this study. Other studies find that biotite breakdown initiates at higher temperatures than this (e.g., (Kunz et al., 2022; Sallet et al., 2023; Weinberg & Hasalová, 2015)). Therefore, we do not consider biotite melting as a significant driver of melt production.

Table 6.5: Scenarios involving melting of micaceous material relative to the quantity of K ₂ O, FeO and MgO necessary to precipitate a pegmatite with 19.4% muscovite and 7.6% biotite.							
Scenario	Oxide	Minimum Required Melt Abundance (Wt% Oxide)	% Liquid Fraction			Calculated Melt Abundance	
			Bt	Ms	Sum		
Scenario 1	K ₂ O	2.70	0	89	89	K ₂ O	10.14
	FeO	1.97	0	89	89	FeO	1.99
	MgO	0.84	0	89	89	MgO	1.21
Scenario 2	K ₂ O	2.70	10	16	26	K ₂ O	2.81
	FeO	1.97	10	16	26	FeO	2.58
	MgO	0.84	10	16	26	MgO	1.12
Scenario 3	K ₂ O	2.70	28	0	28	K ₂ O	2.75
	FeO	1.97	28	0	28	FeO	6.22
	MgO	0.84	28	0	28	MgO	2.52
Scenario 4	K ₂ O	2.70	20	7	27	K ₂ O	2.76
	FeO	1.97	20	7	27	FeO	4.60
	MgO	0.84	20	7	27	MgO	1.89
Scenario 5	K ₂ O	2.70	0	23.74	23.74	K ₂ O	2.70
	FeO	1.97	0	23.74	23.74	FeO	0.53
	MgO	0.84	0	23.74	23.74	MgO	0.32

Pertinent to this system, the role of accessory phases and garnet must therefore be considered. Melting of accessory phases provides a key mechanism for the liberation of certain elements. Accessory phases have been shown to affect geochemistry (e.g., LREE (Inger & Harris, 1993). K is not held in notable quantities in any of the minor phases, and therefore K provides important insight into the role of mica in the melting fraction. However, FeO and MgO are available in Garnet and many of the accessory phases (Epidote, Chlorite, Ilmenite etc). Thus, it is possible that the micas need to just liberate sufficient K, whilst Fe and Mg contents could be supported by melting of less-abundant phases. With temperature constraints limiting the capacity for biotite melting, Scenario 5 identifies the minimum amount of muscovite melting to provide the necessary quantity of K only. Within Scenario 5, accessory phases/garnet would have to contribute 1.44wt% FeO and 0.52wt% MgO to satisfy the KFM system (2.7wt% K₂O, 1.97wt% FeO and 0.84 wt% MgO), together with other non-KFM phases. We therefore postulate the following melting reaction:



This reaction is principally fluid-present muscovite dehydration melting (No.6 (Table 6.4)), but with the inclusion of Fe- and Mg-bearing phases (epidote, chlorite and ilmenite). These are included to facilitate sufficient enrichment in Fe and Mg for the precipitation of the pegmatite.

Trace Elements

An alternative approach to constraining the relative importance of phases in the melting reaction is to use trace elements partitioned into the major phases plagioclase, biotite and muscovite. Mass balance equations were set up to consider the four principal phases within the Alpine Schist & Mataketake Pegmatites (Table 6.6): Plagioclase (plag), Muscovite (ms), Biotite (bt), and Quartz (qtz). As the concentration of each of the elements is known within plagioclase, biotite, and muscovite (Section 5), and with the assumption (as outlined above) that quartz hosts negligible Sr, Ba, Pb and La contents, the equations can be simplified so that d is removed. Here, $C_{i(l)}$ is the composition of the melt (assumed to be equivalent to the pegmatite 1(B)MP and calculated using partition coefficients from the literature, whilst a.plag, b.bt, c.ms and d.qtz refer to the composition and abundances respectively of these phases found in the pegmatite 1(B)MP.

Table 6.6: Modelled equations for melt composition.

Sr	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$
Ba	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$
Pb	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$
La	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$

Scenarios were modelled with consideration of relevant melting reactions (Table 6.4). These reactions are generally concerned with fluid-present melting in the temperature range of 620-700 °C. H₂O-fluxed melting consumes a greater proportion of plagioclase than muscovite due to increasing H₂O activity depressing the plagioclase + quartz solidus more than it decreases the stability of micas (Conrad et al., 1988; Patiño Douce & Beard, 1996; Patiño Douce & Harris, 1998). The plagioclase melting proportion was therefore maintained greater than muscovite (Table 6.10). Biotite liquid contents were often kept at 0, as the temperature constraints mean that biotite melting is limitedly feasible (Section 6.1.2).

Silicic melts have apparent plagioclase-melt partition coefficients (K_d) in the general range of 1 – 13 for Sr (Bacon & Druitt, 1988; Bea et al., 1994; Ewart & Griffin, 1994; Nash & Crecraft, 1985; Streck & Gruner, 1997), although Nash and Crecraft (1985) report a K_d high of 33. For Ba, apparent partition coefficients are between 0.19 (peraluminous melt (Bea et al., 1994)) and 19.55 (high silica rhyolite (Streck & Gruner, 1997)), but typically lie between 0.19 and 3.3 for Ba. For Pb, K_d values lie between 0.31 and 2.2, with the majority within the range of 0.3 and 1.0 (Bea et al., 1994; Ewart & Griffin, 1994; Leeman, 1979; Nash & Crecraft, 1985). La ranges from 0.07 (high silica rhyolite (Streck & Gruner, 1997)), to 4.61 (peraluminous melt (Bea et al., 1994)). Most La K_d range from 0.07 to 0.45. These apparent partition coefficients are quoted for temperatures similar to those within this study, (~800-900°C for rhyolitic magmas, ~750°C for peraluminous granitic melt).

The range of apparent partition coefficients used are stated below in Table 6.7 (all of which are used to establish a range of possible melt concentrations):

<i>Table 6.7: Range of apparent plagioclase-melt partition coefficients.</i>				
Element	<i>kd</i> Low	<i>kd</i> Median	<i>kd</i> High	<i>kd</i> Highest
Sr	1	7	13	33
Ba	0.19	1.745	3.3	19.55
Pb	0.3	0.65	1	2.2
La	0.07	0.26	0.45	4.61

Applying this range of apparent partition coefficients to the trace element concentrations within plagioclase (Table 5.15) yields the following melt concentrations (Table 6.8). The principal takeaway from Table 6.8 is the extreme range in values for all 4 elements, highlighting the uncertainty in partitioning calculations.

<i>Table 6.8: Range of trace element melt concentrations calculated using a range of apparent partition coefficients (see Table 6.7 for Kd)</i>				
Element	Calculated Melt Contents (ppm)			
	<i>Kd</i> low	<i>Kd</i> med	<i>Kd</i> high	<i>Kd</i> highest
Sr	504.79	72.11	38.83	15.30
Ba	324.24	35.30	18.67	3.15
Pb	75.12	34.67	22.54	10.24
La	14.40	3.88	2.24	0.22

Satisfying the Sr, Ba, Pb, La System with Apparent Kd Coefficients

With the range of values calculated from Kd coefficients obtained from the literature, the mass-balance modelling may be written:

<i>Table 6.9: Modelled equations for melt composition (ppm), using apparent K_d Coefficients from the literature (Table 6.8)</i>		
<i>Sr</i>	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$	$15.3 \leq x \leq 504.8 = 740.9a + 2.4b + 30c + 0d$
<i>Ba</i>	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$	$3.2 \leq x \leq 324.2 = 51a + 985.8b + 2607.4c + 0d$
<i>Pb</i>	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$	$10.2 \leq x \leq 75.1 = 33.8a + 3.2b + 7.6c + 0d$
<i>La</i>	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$	$0.22 \leq x \leq 14.4 = 0.3a + 4.3b + 0.02c + 0d$

Table 6.10: Melt scenarios for the apparent partition coefficient obtained from literature. *denotes very close to satisfying system.

Scenario	Element	Calculated Melt Abundance from Plagioclase Apparent Kd (ppm)	% Liquid Fraction					Mass-Balance Calculated Abundance		Systems Satisfied
			Plag	Bt	Ms	Qtz	Sum			
Scenario 1	Sr	$15.3 \leq x \leq 504.8$	9	0	1	90	100	Sr	66.981	Sr
	Ba	$3.2 \leq x \leq 324.2$	9	0	1	90	100	Ba	30.664	Ba
	Pb	$10.2 \leq x \leq 75.1$	9	0	1	90	100	Pb	3.118	
	La	$0.22 \leq x \leq 14.4$	9	0	1	90	100	La	0.025	
Scenario 2	Sr	$15.3 \leq x \leq 504.8$	49.5	0	0.5	50	100	Sr	366.9	Sr
	Ba	$3.2 \leq x \leq 324.2$	49.5	0	0.5	50	100	Ba	38.3	Ba
	Pb	$10.2 \leq x \leq 75.1$	49.5	0	0.5	50	100	Pb	16.8	Pb
	La	$0.22 \leq x \leq 14.4$	49.5	0	0.5	50	100	La	0.13	
Scenario 3	Sr	$15.3 \leq x \leq 504.8$	67	0	10	22	100	Sr	499.7	Sr
	Ba	$3.2 \leq x \leq 324.2$	67	0	10	22	100	Ba	321.0	Ba
	Pb	$10.2 \leq x \leq 75.1$	67	0	10	22	100	Pb	23.5	Pb
	La	$0.22 \leq x \leq 14.4$	67	0	10	22	100	La	0.18	*
Scenario 4	Sr	$15.3 \leq x \leq 504.8$	40	5	10	45	100	Sr	299.5	Sr
	Ba	$3.2 \leq x \leq 324.2$	40	5	10	45	100	Ba	330.4	*
	Pb	$10.2 \leq x \leq 75.1$	40	5	10	45	100	Pb	14.4	Pb
	La	$0.22 \leq x \leq 14.4$	40	5	10	45	100	La	0.32	La
Scenario 5	Sr	$15.3 \leq x \leq 504.8$	33.5	7.6	19.4	39.5	100	Sr	254.2	Sr
	Ba	$3.2 \leq x \leq 324.2$	33.5	7.6	19.4	39.5	100	Ba	597.8	
	Pb	$10.2 \leq x \leq 75.1$	33.5	7.6	19.4	39.5	100	Pb	13.0	Pb
	La	$0.22 \leq x \leq 14.4$	33.5	7.6	19.4	39.5	100	La	0.31	La
Scenario 6	Sr	$15.3 \leq x \leq 504.8$	48.5	0	29	22.5	100	Sr	368.0	Sr
	Ba	$3.2 \leq x \leq 324.2$	48.5	0	29	22.5	100	Ba	780.9	
	Pb	$10.2 \leq x \leq 75.1$	48.5	0	29	22.5	100	Pb	18.6	Pb
	La	$0.22 \leq x \leq 14.4$	48.5	0	29	22.5	100	La	0.137	

Table 6.10 shows melting scenarios that generate apparent melt compositions of trace elements. This modelling intends to showcase the extent to which differing scenarios satisfy melt compositions inferred from trace element contents of plagioclase in the pegmatite. Disparate from previous scenarios, where high quartz melt fraction was required to approximate melt contents to those calculated, these scenarios communicate otherwise. For example, scenario 1 considers a melt comprised of 90% quartz, however, this melt does not satisfy Pb or La. This communicates the necessity for plagioclase and muscovite to melt to liberate sufficient Pb and La. Scenario 2 considers a melt dominated by quartz and plagioclase. All elements are satisfied in this scenario, apart from La. Scenario 3 considers a melt comprised of 67% plagioclase, 22% quartz and 10% muscovite. All scenarios, bar La, are again satisfied here, although the system is close to providing sufficient La. Scenario 4 is a quartz and plagioclase dominated melt (85% combined), with 10% muscovite and 5% biotite. This scenario almost satisfies all elements, with Ba edging above the upper limit. This communicates how excess mica can result in too much Ba to satisfy the modelling. Despite temperature constraints generally removing the possibility for biotite melting, we have included a small amount of biotite breakdown in Scenario 4, as the melting reaction No.4 (Table 6.4) allows for a small portion of biotite to breakdown (Clemens et al., 2020; Mayne et al., 2020). Scenario 5 involved

the melting fractions of plagioclase, muscovite, and biotite equal to those for the pegmatite (*Section 5.1*), however due to the high Ba contents in analysed micas, the Ba concentrations in the melt are too high. This communicates that these four phases do not accurately reflect trace element contents and are not the sole determinants of these trace elements. Scenario 6 applies the melt proportions for fluid-present muscovite melting from Patiño Douce and Harris (1998), however this does not satisfy the Ba system. Again, this is due to the elevated Ba contents in muscovite, resulting in the melt containing too much Ba.

Further insights can be gained from combining the trace element discussion with the KFM calculations. As highlighted previously, sufficient KFM must be liberated to precipitate a pegmatite with 19.4% muscovite, and 7.6% biotite. Previous modelling communicated that either a very high portion of muscovite (89%) must melt to provide sufficient KFM, a mixture of muscovite and biotite must melt to provide enough KFM, or accessory phases also contribute to KFM. As the first two scenarios are non-feasible (Table 6.5; 89% muscovite melt would not produce the observed pegmatite composition, and temperature constraints allow for biotite melting to be discounted), we suggest the possibility for accessory phases to have contributed to the KFM system. We also propose the same approach for the trace element modelling in this section. La is contained in monazite and epidote of the Alpine Schist; monazite contains 13.83wt% La_2O_3 and epidote contains 0.46wt% La_2O_3 .

Therefore, the breakdown of these phases, even in small proportions, would contribute to La. SEM-EDS returned no measurable Sr, Ba and Pb within minor phases (*Section 5.1.2*). Therefore, if the breakdown of accessory phases is considered, it is solely the La system that is directly affected by accessory phases (within this trace-element modelling). Consequently, scenarios 2, 3 and 6, which all provide insufficient La, may in fact be feasible (Table 6.10). Scenarios 2 and 3 would then satisfy all four trace elements. These scenarios involve a quartz-plagioclase dominated melt, with some muscovite melting. This aligns with temperature constraints (low temperature melting favours plagioclase breakdown over muscovite (Patiño Douce & Harris, 1998)), and compositional variation between 1.AS and 1(B)MP (the latter is enriched in quartz and feldspar, indicating these dominated the melting process (*Section 6.1.1.1*)). A quartz-plagioclase dominated melt is indicative of water-present melting, as the quartz-plagioclase solidus is depressed much more intensely than the stability of muscovite when H_2O is present (reference Conrad paper and others). Briggs and Cottle (2018) propose the following four reactions for the formation of the Mataketake Pegmatites (Table 6.4): (1) *quartz + plagioclase (ab) + K-feldspar (or) + H_2O = melt*; 2) *muscovite + plagioclase + quartz + H_2O = melt*; 3) *garnet + biotite + H_2O = garnet + biotite + melt*; 4) *quartz + K-feldspar + plagioclase + H_2O = plagioclase + melt* (see Briggs and Cottle (2018) and references therein). With reactions 1 and 4 previously discounted within this study due to the absence of K-feldspar in analysed samples (*Section 6.1.3.1*). We are left with reactions 2 and 3. Biotite melting requires high temperatures ($\sim 700^\circ\text{C}$ (Kunz et al., 2022; Sallet et al., 2023; Sawyer, 2010; Watkins et al., 2007;

Weinberg & Hasalová, 2015)). Reaction 3 can therefore be discounted, due to the high temperatures necessary for biotite breakdown (in any significant proportion) not being reached. This modelling supports a fluid-present muscovite melting reaction, (reaction No.2 from Briggs and Cottle (2018)), with additional Fe and Mg being liberated by accessory phases; producing Reaction No.9 ($Ms + Qtz + Plag (Ab) + H_2O \pm (garnet) \pm (epidote) \pm (monazite) \pm (chlorite) \pm (ilmenite) = melt$).

Another possibility is that the melting reaction $quartz + plagioclase + H_2O = melt$ may have contributed to melt production (Clemens et al., 2020; Mayne et al., 2020). This reaction would also consume a small portion of muscovite/biotite and is therefore similar to the reaction identified above. Scenario 2 involves a quartz + plagioclase dominated melt, with a minute portion of muscovite (Table 6.10). Within this scenario, all trace elements apart from La are satisfied. Hence, if we assume La contents are dictated by accessory phases, this scenario is feasible. This low temperature reaction (<650°C (Clemens et al., 2020; Mayne et al., 2020)), agrees with temperatures calculated within this study. However, we have shown how 23.7% muscovite needs to melt for sufficient K to be liberated. Whilst assuming Fe and Mg can be liberated by accessory phases, whilst K is only contained in micas. Consequently, as this reaction does not satisfy K, we maintain that the following reaction No.9 produced the Mataketake Pegmatites. This reaction is a refined version of the fluid-present muscovite dehydration reaction, which includes garnet and accessory phases, which will have contributed Fe, Mg and trace elements like La.

We now model the lithium composition within the melt, building on previous work of Koopmans et al. (2023).

Melt Composition; Lithium

Following the work of Koopmans et al. (2023), this study intends to provide a real case study example to modelled scenarios. Plagioclase could not be used for mineral-melt partitioning calculations on lithium, as the plagioclase data for the pegmatite was all below LOD of 1.39ppm for lithium (apart from 2 analyses). It was therefore decided to calculate melt Li contents using the muscovite and biotite from the pegmatite. Mineral-melt partition coefficients were the same as those used in Koopmans et al., (2023), as summarised in Table 6.10. The second partition coefficient for biotite was also used from Icenhower and London (1995), to reflect the uncertainty within partitioning calculations (Table 6.10).

Mineral	Ci(C) ppm	Ci(l) ppm	Partition Coefficient (mineral-melt)	Reference
Muscovite	40.63	49.55	0.82	(Icenhower & London, 1995; Koopmans et al., 2023)
Biotite	177.18	106.10	1.67	(Icenhower & London, 1995; Koopmans et al., 2023)
Biotite	177.18	221.48	0.80	(Icenhower & London, 1995)

Table 6.11: Mineral-melt partitioning calculations for muscovite and biotite data obtained from Laser ICP-MS. The top two partition coefficients are the same as those used by Koopmans et al., (2023). Ci(c) = average Li concentration in each phase (recorded using LA-ICP-MS (Tables 5.16 & 5.17). Ci(l) = calculated Li melt concentration using partition coefficients in this table.

The calculated Li abundance in the melt that precipitated the pegmatite averaged 49.55ppm when using muscovites, and 106.10ppm and 221.48ppm when using biotites for calculations. The following equations could then be set up for lithium:

$Li_{\text{muscovite}}$	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$	$49.55 = 1.96a + 165.71b + 46.37c + 0d$
Li_{biotite}	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$	$106.10 = 1.96a + 165.71b + 46.37c + 0d$
Li_{biotite2}	$C_{i(l)} = a.plag + b.bt + c.ms + d.qtz$	$221.48 = 1.96a + 165.71b + 46.37c + 0d$

Table 6.12: Expressions for mass-balance modelling where a , b , c & d are the modal abundances of plagioclase, biotite, muscovite and quartz respectively. Liquid contents (Li) calculated using partition coefficients in Table 6.11. Coefficients for each phase taken from average Li abundance in Alpine Schist in each phase. The 2 different equations correspond to calculated melt contents from muscovite and biotite.

The mineralogical compositions of both 1.AS and 1(B)MP means that micas are the most important mineral for lithium; they are the only phases that make up a significant portion of both rocks and that can host lithium in significant quantities. There is no solution to the third expression; a melt comprised solely of biotite with the composition of that in 1.AS would only contribute 165.71ppm Li. Hence, this partition coefficient does not seem applicable. The other expressions necessitate a significant micaceous melting portion for the expressions to be satisfied. For even the lower end of 49.55ppm Li in the melt, this requires a melting fraction of around 40% muscovite and 20% biotite. If we alter this 60% micaceous melting portion to 50% muscovite, 10% biotite, with 20% quartz and 20% plagioclase, 40.15ppm Li would be liberated. Therefore, this modelling appears to evidence a notable biotite melting portion to liberate sufficient Li. Previously (Section 6.1.2), temperature constraints on the formation of 1(B)MP meant that biotite melting, in any significant quantity was discounted. However, the expressions above require a biotite melting component. A melt made up of purely muscovite, would only provide 46.37ppm Li in the melt. These results therefore suggest that a large portion of the melting fraction was comprised of micas.

6.1.3.3 Limitations to the Applicability of Equilibrium Melting Models

Geochemical modelling within Section 6.1.3.2 suggests conflicting information. The KFM system suggests a biotite melting component, whereas temperature constraints discount biotite melting. Modelling for Sr, Ba, Pb and La suggested a necessity for plagioclase and muscovite to liberate Pb and La, and a limitation on mica melting due to excessive Ba. Additionally, La is contained in extremely small quantities in plagioclase, muscovite and biotite, and is therefore difficult to model. Within both modelling scenarios (KFM & trace elements), we then considered accessory phases, which can contribute Fe, Mg and La to the melting fraction. This enabled us to confine the melting reaction (considering all previous sections of this Chapter), to Reaction No.9 (Section 6.1.3.2). However, modelling for Li, then suggested a notable biotite melting portion. These issues show a discrepancy between the modelled systems and the case study. Although the use of trace elements as proxies in many geological systems provides crucial insight which otherwise may not be realised, their applicability in crustal anatexis and limitations specific to this case study must be critically considered.

Firstly, this study assumes that 1.AS is analogous to the protolith that formed 1(B)MP. However, the Alpine Schist is known to vary in composition, due to its protolith (Torlesse Terrane), being varied in its composition. Therefore, the observed mineralogy in 1.AS, and the respective geochemistry, may not accurately reflect the composition of the melt source for 1(B)MP. For example, 1.AS.H is mineralogically different to 1.AS, as it contains calcite. Additionally, previous literature observes K-feldspar as a major constituent in the Alpine Schist (Wallace, 1974), whereas it is not recorded in this study.

Secondly, equilibrium melting models have their ability to predict trace element melt contents dictated by their adherence to the following properties: Henry's Law (concerning solubility of volatiles), all phases in the source-rock being "equally accessible" to melt, and finally that kinetic effects exert minimal influence on re-equilibration and solid-melt partitioning processes (Bea, 1996). However, crustal magmas often contain accessory phases rich in trace elements, and crustal anatexis commonly occurs at low temperatures (particularly in this case study). Consequently, crustal melts rarely satisfy these requirements.

Within equilibrium melting models, there are four principal controls on trace element concentrations in melts (Bea, 1996):

1. Source rock composition; both chemical and mineralogical
2. Modal abundance of phases melting
3. Extent of partial melting
4. Crystal-melt partition coefficients

The mode of occurrence of trace elements governs their partitioning behaviour (Bea, 1996). Within accessory phases, trace elements can be essential structural components (e.g., zirconium in Zircon), whereas other trace elements can occur in ‘trace’ quantities within major phases (e.g., V/Cr in micas). In this second mode of occurrence, intracrystalline diffusion for some elements (e.g., Li, Rb, Cs, Sr, Ba, Ga, and Pb) is limited due to the low temperatures of crustal anatexis, resulting in near-unity crystal-melt partition coefficients (Bea, 1996). Consequently, mass balancing of proportions of melted material versus crystallised material principally determines melt abundances. Alternatively, elements like P, La, Sm, Nd and Zr (that are primarily hosted as essential components in accessory phases), display more complex partitioning behaviour due to: grain size variation, textural positioning of accessory phases, solubility constraints, and dissolution kinetics (Bea, 1996). This leads to greater variability in their distribution during melting.

As this modelling only considers the four principal phases in both the schist and pegmatite, the role of accessory phases is ignored. However, within the KFM and trace element modelling, accessory phases may contribute to the budget of modelled elements. For example, within the trace element modelling, elements like lanthanum are much more abundant in accessory phases (e.g., epidote, monazite (Section 6.1.3.2) than in major phases, and therefore their use within this system is limited. Consequently, is it possible that the lack of accessory phases in this modelling may reduce the significance of the modelling, particularly for trace elements. The melt abundance of La is dominantly controlled by its solubility in melts and kinetics of dissolution from the host rock rather than conventional crystal-melt distribution coefficients (see references within Bea (1996)). Additionally, many of the values obtained for La were below limits of detection (LOD) for the pegmatite specimen. This reflects how La is depleted in plagioclase, and hence may not give a holistic picture of the La system.

The rate of melt segregation plays a vital role in trace element behaviour (Icenhower & London, 1995). A low segregation rate, where melt remains in contact with restitic solids, allows sufficient time for re-equilibration to occur; this is known as batch-melting (Bea, 1996). Conversely, a rapid rate of melt segregation inhibits melt-solid equilibration; this is known as fractional or Rayleigh-type melting (Bea, 1996). Bea (1996) refers to both as equilibrium melting because the effective partition coefficients are equivalent to their equilibrium values.

Therefore, deviation of trace element abundances from those predicted by equilibrium melting models are common. For low temperature melting scenarios, like this case study, Bea (1996) communicates how these “rarely” align with equilibrium melting models. There are difficulties with including accessory phases within these models: they may be preferentially concentrated proximal to/within certain phases, and the variability in textural occurrence of certain accessory phases may have

tangible effect on trace element partitioning. Despite being able to include accessory phases within equilibrium models, discrepancies are still the expectation, not the exception.

Within this system, the Sr, Ba, Pb, and La contents of quartz are assumed to be negligible (0). However, analysed elements may be contained within quartz. For example, Nash and Crecraft (1985) give the following partition coefficients for Ba in quartz: 0.015 ± 0.003 , 0.004 ± 0.0009 , 0.011 ± 0.013 , 0.06 ± 0.0005 . These average out to a partition coefficient of 0.09. Neutron activation analyses of quartz gave Ba contents up to 7.1ppm (Nash & Crecraft, 1985), communicating the possible error introduced by assuming the Sr, Ba and Pb contents of quartz to be 0. Although the quartz analyses done by Nash and Crecraft (1985) are within silicic magmas, it highlights that trace elements can be held within quartz at concentrations that have tangible effect on bulk melt contents and partitioning.

Petrographic analyses of the pegmatite revealed protomylonitic textures: sub-grain quartz deformation, elongation of quartz grains relative to foliation, ‘smearing’ of micas, bookshelf fracturing of feldspar porphyroblasts, and mica ‘fish’, amongst other textures. These are interpreted as representative of post-emplacement deformation, detailed in Chapter 4. This second stage of deformation may have influenced the Sr, Ba, Pb and La geochemical systems by reequilibration, alteration or lattice dislocations facilitating enhanced dissolution of trace elements. Diffusion of trace elements in major phases is another pertinent factor. Yund et al. (1989) highlight how dislocations, particularly of deformative origin, can enhance diffusion of trace elements. Diffusion is also enhanced along regions of “high crystal defect density” (Hodges & Bowring, 1995); as shown by Hodges and Bowring (1995) for ^{40}Ar . As such, the shearing, elongation and fracturing of crystals during post-emplacement deformation may well have had a tangible effect on trace element diffusion.

There are many limitations and assumptions specific to this basic mass-balance modelling: it only considers the four key phases, calculated melt abundance is based solely on plagioclase, it is assumed that plagioclase precipitated early on, there is chemical variability and analytical uncertainty within the three analysed phases (muscovite, biotite + plagioclase), it is assumed that the current geochemistry of the phases accurately reflects the original composition (i.e., there has been no geochemical modification or alteration), amongst many other assumptions.

Sr, Mn, Rb, Fe and Ba are concentrated over 100 times in springs of South Island (New Zealand) relative to surface waters (Menzies, 2012). Menzies also notes that Li, B, Rb, Mn, Sr, Cs and Ba are positively correlated with estimated silica equilibration temperatures. This suggests that reaction temperatures have a strong control on the quantities of these elements that may be leached from host rocks. The enrichment of these fluid mobile elements in sample locations close to the Mataketake region, such as Welcome Flat Spring, highlights the possibility that the analysed amphibolite schist and pegmatite are depleted in these elements. However, as discussed in Chapter 4, we do not see significant evidence of hydrothermal alteration. This is supported by the lack of variance in intragrain

analyses (we would anticipate grain rims to be distinct from cores if hydrothermal alteration had affected them).

Perhaps the most significant takeaway, is that the intersection of melting rate and intracrystalline diffusion may have caused effective trace-element crystal-melt partition coefficients to be “equal to or near unity” (Bea, 1996), and as such, crustal melting may occur as disequilibrium melting. In this case, trace element concentrations are dictated simply by mass balance of the composition and proportion of phases that melt. The limitations in this section have some effect on major element contents, however major element melt contents are principally dictated by major phases. Therefore, accessory phases have a limited effect on major elements. However, we propose the necessity for the breakdown of some accessory phases (Reaction No.9), to provide sufficient Fe and Mg (Section 6.1.3.2). If trace-element partition coefficients were approximated to unity ($D_i = 1$), and calculated whole-rock abundances for the pegmatite were used as the required melt contents produced from the schist, then required trace element melt contents would be: 724.6ppm Ba, 175.8ppm Sr, 8.7ppm Pb, 0.3ppm La, and 21.5ppm Li. These concentrations of Sr and La are contained within the bounds of geochemical modelling done in this study (Table 6.10). However, the Ba value is significantly above the range of melt contents calculated from apparent partition coefficients (upper bound was 324.2ppm), and Pb and Li values are below ranges used in geochemical modelling (Table 6.10 & 6.11). These values for melt contents facilitate a higher proportion of muscovite melting for Ba and mean that a biotite melting fraction is no longer necessary to satisfy modelled Li contents. Although aspects of the approach to modelling are flawed, the geochemical modelling in section 6.1.3.2 highlights the necessity for the involvement of mica in the melting reaction, and modelling of Li abundances underlines the importance for biotite melting to enrich Li melt contents. This section also communicates the necessity for further research into partitioning behaviour in low-temperature, crustal anatexis, including quantifying the effects of accessory phases, and the extent to which deformation affects geochemistry.

6.1.4 Summarising Melt Reactions and Processes

Considering all evidence within this study and existing literature we conclude that the Mataketake Pegmatites formed via a low-temperature, fluid-present muscovite dehydration partial melt. We propose a reaction like the second proposed by Briggs and Cottle (2018), however we include accessory ferromagnesian phases and garnet as our modelling communicates the necessity for accessory phases to liberate Fe + Mg. Our proposed reaction (Reaction No.9) is:



In the subsequent section (6.2) we link our proposed melting reactions and processes to metal enrichment.

6.2 How does this link to metal enrichment.

The Mataketake Pegmatites formed via fluid-present melting, with temperatures exceeding 539°C (minimum temperature of This Study), and possibly up to ~700°C (Beyssac et al., 2016). These conditions preclude biotite melting, which requires >740°C (Kunz et al., 2022; Weinberg & Hasalová, 2015). Major element geochemistry shows that muscovite melting is essential to liberate sufficient K₂O, FeO, and MgO. Here, we evaluate how the proposed melting reaction (Reaction 9) explains the lack of metal enrichment in this natural pegmatite system and consider the implications for enrichment mechanisms more generally. This section focuses particularly on Li and Sn (two metals of economic interest), and also seeks to add new constraints on processes addressed by recent studies, particularly Koopmans et al. (2023) and (Kunz et al., 2022).

Pegmatites are key sources of critical metals such as Li, Be, V, Co, Nb, In, Cs, Sn, Ta, and W (Kunz et al., 2022), however the reactions and processes that enable the release and concentration remain imperfectly constrained (Černý et al., 2012; Gardiner et al., 2024; Knoll et al., 2023; Koopmans et al., 2023; Kunz et al., 2022). In particular, there is a lack of literature constraining enrichment processes, particularly in low-temperature, small-scale partial melting scenarios (such as this case study). The Mataketake Pegmatites provide a scenario where enrichment did not occur, facilitating a process-based assessment of limiting factors.

The metals associated with pegmatites are commonly held in micas, which therefore provide a mechanism for sequestering, concentrating, and/or mobilising these elements during crustal melting. For example, Kunz et al. (2022) show the importance of biotite in liberating Li. There are variable theories as to the formation of LCT-pegmatites. Amongst these, and pertinent to this study, are small degree anatectic melts (Gardiner et al., 2024; Koopmans et al., 2023), which may include minimum-temperature muscovite melting (Černý, 1991; Romer & Kroner, 2016; Romer & Kroner, 2015).

6.2.1 Lithium

Hosts and Controls

Within metamorphic rocks, biotite, muscovite, cordierite and staurolite are the principal hosts of Li (Knoll et al., 2023; Koopmans et al., 2023; Kunz et al., 2022; Simons et al., 2017). Consequently, the breakdown of these minerals and the extent of reequilibration with restitic phases controls partitioning of elements, and is a key control on Li and other critical elements (Koopmans et al., 2023; Kunz et al., 2022). Conversely, the preservation of micas during anatexis inhibits melt Li enrichment, as Li is not released into the melt (Koopmans et al., 2023).

Observations from This Study

The samples studied here are lacking in cordierite and staurolite; micas are therefore the most important phases for Li within this case study. The Alpine Schist and Mataketake Pegmatites are not

enriched in lithium. Across analysed samples, biotites average 200ppm Li, and muscovites average 43ppm Li. Whole-rock Li decreases from schist to pegmatite: 34.7ppm in 1.AS, to 21.5ppm in 1(B)MP, calculated from measured Li in plagioclase, muscovite, and biotite (Tables 5.15-5.17) and assuming quartz $\approx$ 0ppm Li.

Modelled Li-in-melt contents for the Mataketake pegmatites were 50-222ppm (Section 6.1.2; Table 6.11). This is significantly less than the 5000ppm required for the precipitation of Li-aluminosilicates, e.g., spodumene, lepidolite, or petalite (Koopmans et al., 2023; London, 1984; Maneta et al., 2015).

Why Li Enrichment is Limited Here

H₂O-present melting limits Li concentration in melts “under all conditions” (Koopmans et al., 2023). This is attributed to much less breakdown of mica via melting reactions at the point of extraction (Koopmans et al., 2023), consistent with greater extents of plagioclase $\pm$ quartz melting than muscovite (effectively diluting the melt), as the plagioclase $\pm$ quartz solidus is further depressed (Patiño Douce & Harris, 1998). This aligns with the proposed fluid-present reaction (No. 9), and the lack of Li enrichment in this study.

Kunz et al. (2022) demonstrate that biotite dehydration melting is pivotal in melt enrichment of Li, as it hosts Li in significant quantities and can be important in liberating the alkali metal. As high-temperature biotite melting has not occurred in the Mataketake Region (Sections 6.1.1, 6.1.2, 6.1.3, 6.1.4), then it is possible that Li has largely remained ‘sequestered’ in solid biotite of the Alpine Schist during melting, resulting in Li melt contents remaining low. This is consistent with the calculated Li whole-rock concentrations decreasing, rather than increasing, from 35ppm to 22ppm from the schist to the pegmatite.

Role of Fractional Crystallisation

Fractional crystallisation can also enrich melts in incompatible elements (Bradley & McCauley, 2013; Bradley et al., 2017; Černý et al., 2005; Černý, 1991; Černý & Ercit, 2005; Černý et al., 2012; Cerny et al., 1985; Duuring, 2020; Gardiner et al., 2024; Knoll et al., 2023; Koopmans et al., 2023). However, the Mataketake Pegmatites represent a very low-melt fraction that has experienced negligible fractionation.

Generally, alkali elements in muscovites increase in concentration with increasing fractionation (Cerny et al., 1985; Wise et al., 2024). Černý et al. (2005) states that extreme fractional crystallisation is responsible for most rare metal mineralisation within fractionated granites. This is consistent with much higher Li concentrations in biotite and muscovite from the Cornubian batholith (typically 2000-5000ppm, E.Richmond, personal communication). Consequently, the lack of fractionation within the highly localised, small scale Mataketake Pegmatites is a likely contributing factor to the lack of Li-enrichment.

Comparison with Two-Stage Anatexis Model

Koopmans et al. (2023) cover flux and dehydration melting in relation to the formation of Li-rich pegmatites. To achieve melt concentrations sufficient to precipitate Li-ore minerals, Koopmans et al. (2023) find that a second stage of anatexis can result in a combined enrichment factor of ~ 14.2 , with their modelled system achieving 7496ppm Li (Figure 6.6). However, this is for dehydration melting, (which includes biotite), and involves temperatures up to $\sim 850^\circ\text{C}$ (Figure 6.6). For fluid fluxed-melting, the same second stage of anatexis produces melts with lower Li contents, up to ~ 4500 ppm (Figure 6.6). This is because higher temperatures are not achieved prior to melt extraction, and therefore less biotite has melted. However, the Mataketake Pegmatites of this study, (which formed by fluid-present (flux) melting), show a depletion in calculated whole-rock Li from the schist to the pegmatite.

This depletion is attributed to insufficient melting of micas, particularly biotite, in this low-T, fluid-fluxed melting scenario (Kunz et al., 2022). Despite our proposed reaction containing muscovite as a key phase, the muscovites of 1.AS only contain 46.4ppm Li, and therefore do not liberate sufficient Li to ‘enrich’ the melt. Figure 6.6 shows figures from Koopmans et al. (2023) showing Li-in-melt contents for metasediment protoliths (A), which then crystallises as a granite. This granite is then remelted and produces the Li-in-melt contents observed in (B). To contextualise this case study, we then plot (purple arrows) our calculated Li-in-melt contents of 49.55ppm, 106.10ppm and 221.48ppm (C_i(l); Table 6.11) covering our proposed temperature range (Section 6.1.2). These arrows show the limited nature of Li-melt-enrichment in this study relative to that of Koopmans et al. (2023), and communicates the necessity for higher temperatures to facilitate Li-enrichment through mica breakdown, particularly that of biotite (Koopmans et al., 2023; Kunz et al., 2022).

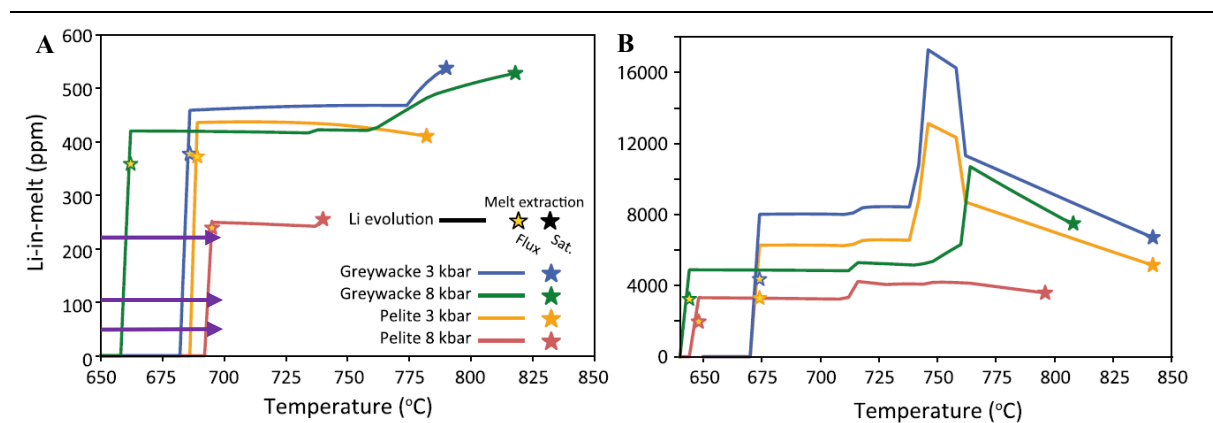


Figure 6.6: Data from this study (purple arrows) are plotted on figure from Koopmans et al. (2023). **A)** Petrologic modelling of Li melt concentrations from metasedimentary protoliths. **B)** Petrologic modelling of the remelting of corresponding granites produced by the four scenarios in A, displaying significant enrichment. The arrows in A illustrate calculated Li melt contents of 49.55ppm, 106.10ppm and 221.48ppm (C_i(l); Table 6.11) and cover our proposed temperature range (539-700°C).

There has been no second-stage of melting in the Mataketake Pegmatites. However, if 1(B)MP were remelted, it would still not achieve concentrations close to those necessary for Li-ore mineral formation. This is because the produced pegmatite (1(B)MP) only attains whole rock Li-contents of 21.5ppm, compared to the initial metasediments in Koopmans et al. (2023) having 125.5ppm. Consequently, this study illustrates the importance of biotite dehydration melting within both stages of melting, for the proposed anatectic origin of economically significant Li pegmatites by Koopmans et al. (2023) to function.

Concise Chronology for Li Enrichment

We propose the following chronology for the formation of Li-enriched pegmatites through 2 stages of crustal anatexis:

- 1) Protolithic metagreywacke/pelite (assume Li concentrations equal to that of Koopmans et al. (2023)).
- 2) Crustal anatexis; extent of micas melting relative to metal-depleted phases (e.g., plagioclase/quartz) will dictate critical element melt contents, with biotite melting the most significant critical element contributor of critical metals to melts of greywacke/schistose compositions (Kunz et al., 2022). As fluid-present melting depresses the plagioclase + quartz solidus to a greater extent than the muscovite solidus, fluid-present melting limits the enrichment of critical metals (can be considered melt ‘dilution’ due to elevated plagioclase + quartz melting). It is therefore favourable to have fluid-absent melting, particularly fluid-absent biotite melting. This requires higher-temperatures; between 850-900 °C for fluid-absent biotite melting (Michaud et al., 2021; Patiño Douce & Beard, 1995; Peterson et al., 1991; Pickering & Johnston, 1998; Sallet et al., 2015; Sallet et al., 2023; Skjerlie & Johnston, 1993, 1996; Thompson, 1982; Vielzeuf & Holloway, 1988). Temperature is also important for increasing the quantity of muscovite melting relative to plagioclase (Patiño Douce & Harris, 1998).
- 3) Assuming liberation of Li (& other critical elements) via biotite melting, or to a lesser extent, muscovite melting, the produced granite/pegmatite will be enriched in critical metals, like Li.
- 4) Remelting of this granite/pegmatite, applying the same principles outlined in stage 2, may result in a melt of sufficient Li-concentration to precipitate Li-ore minerals (Koopmans et al., 2023)

6.2.2 Tin

Hosts and Measured Abundances

Sn is also typically hosted in muscovite and biotite, with concentrations in the typical range of 30-120ppm, but reaching up to 1300ppm in micas from rare metal granites (Breiter et al., 2023; Gardiner et al., 2024). However, biotite in 1.AS and 1(B)MP averaged 1.77ppm and 2.30ppm respectively and

are therefore not enriched (Kunz et al., 2022; Romer & Kroner, 2016). Sn contents were not measured for the muscovites. Kunz et al. (2022) record higher Sn quantities in muscovites than biotites.

Therefore, we are tentative to suggest the implications of our constrained melting reaction on Sn contents, as we do not know muscovite Sn contents, nor whole rock Sn abundance. This is an area for future research.

Accessory Phases and Unknowns

Rutile, ilmenite and titanite are relevant hosts of Sn and W in this case study (Klemme et al., 2006; Kunz et al., 2022; Zack et al., 2002). Rutile, for example, contains up to 128ppm Sn in the garnet-mica schists of Zack et al. (2002). Laser-ICP-MS data were not attained for these accessory phases, and consequently their trace element contents are unknown. Accordingly, we cannot speculate on their role in Sn enrichment/depletion.

6.2.3 Other Metals

The aforementioned metals (Be, V, Co, Nb, In, Cs, Ta, and W) are preferentially hosted in micas (Kunz et al., 2022). This study analysed V, Nb and Cs within both muscovite and biotite, as well as Co in muscovite, and W in biotite. Interestingly, V is absent in the pegmatite micas and concentrated in micas of the Alpine Schist (Figure 5.9 & 5.10). In the Alpine Schist, the biotites average higher V (369 ppm (1.AS) & 470ppm (1.AS.H)), than the muscovites (291 ppm (1.AS)). Cs in micas is noticeably enriched in 1.AS and depleted in 1(B)MP (Table 5.16, 5.17 & Figure 5.9). Cs is more enriched in biotites than muscovites (Tables 5.16 & 5.17; See Section 5.3). Muscovites are depleted in Co in both 1.AS and 1(B)MP, but it is the former that hosts relatively more Co (average 2.60ppm in 1.AS, compared to 1.11ppm in 1(B)MP). W is enriched in biotite of 1.AS and depleted in those of 1(B)MP. Biotites are more enriched in Cr, Mn, Zn, and Rb (Tables 5.16 & 5.17; Section 5.3), whereas muscovite is more enriched in Sc, Ga and Ba (Tables 5.16 & 5.17; Section 5.3). This relative enrichment of V, Cs and W in the Alpine Schist is possibly akin to the observed metal enrichment in residua in migmatites, relative to the crystallised melt (leucosomes) of the Iberian Masif that formed by muscovite melting (Kunz et al., 2022; Wolf et al., 2018). Wolf et al. (2018) attributes this distribution to the continued stability of their host phases during muscovite dehydration melting. This is supported by the mica-hosted trace elements (e.g., Li, V, Cr & Cs) being enriched in the restite (Figure 6.7; Wolf et al. (2018)). Wolf et al. (2018) observe that this difference in metal concentrations between melt (leucosomes) and residua, particularly for elements that concentrate in micas, is not as severe in higher-temperature scenarios, where biotite melting reactions have occurred (Figure 6.7). This indicates that these higher temperature melting reactions (~800°C) are necessary for the liberation of critical metals (Kunz et al., 2022; Wolf et al., 2018). Applying this hypothesis to this case study aligns with our proposed melting theory (Reaction No.9), specifically the lack of biotite breakdown, and geochemical data (showing no enrichment of critical metals).

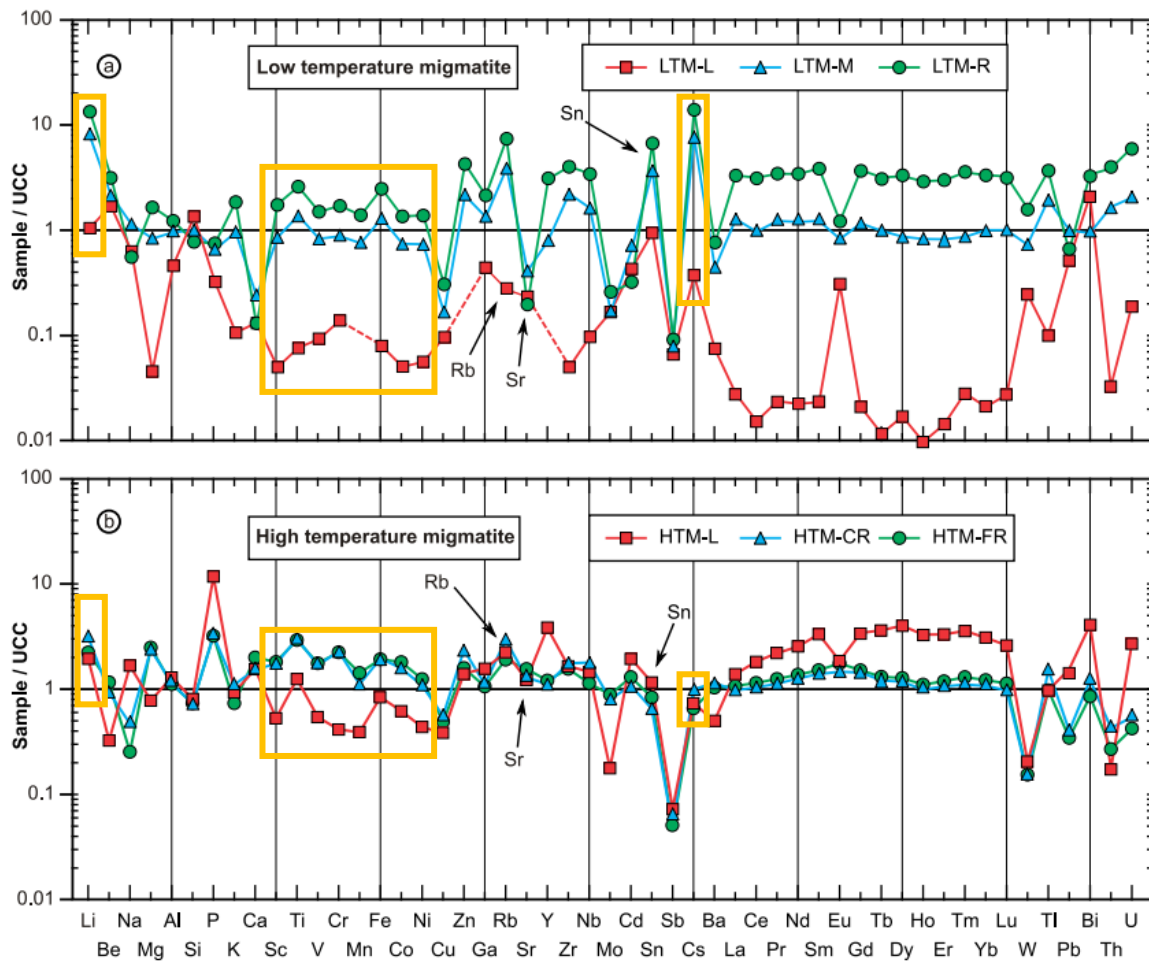


Figure 6.7: From Wolf et al. (2018), showing whole rock analyses of different regions of migmatite samples. **a) (LTM)** Low temperature migmatite ($\leq 740^{\circ}\text{C}$). LTM-L, LTM-M, & LTM-R = Leucosome, melanosome, and mesocratic residuum **b) (HTM)** High temperature migmatite ($\leq 850^{\circ}\text{C}$). HTM-L, HTM-CR & HTM-FR = Leucosome, coarse-grained residuum, and fine-grained residuum. Orange boxes show key differences between LTM and HTM.

6.2.4 Metal enrichment; Synthesis and Implications

Metal enrichment in pegmatites depends on the melting reaction, temperature, and water availability, alongside fractionation and the rate of melt segregation (which controls the effective partition coefficients). In the Mataketake Pegmatites, fluid-present, low-temperature melting promoted plagioclase- and quartz- rich melt production, limited mica breakdown, and negligible fractionation. All these collectively suppressed the enrichment of Li, Sn, and other mica-hosted metals (Černý & Ercit, 2005; Černý et al., 2012; Gardiner et al., 2024; Koopmans et al., 2023; Kunz et al., 2022; Patiño Douce & Harris, 1998; Wolf et al., 2018). This case study highlights that biotite dehydration melting at higher temperatures is a necessary condition for significant Li enrichment, and that two-stage anatexis only yields ore-forming Li if the starting Li budget and mica breakdown are sufficient.

7 SYNTHESIS AND CONCLUSIONS

Our concluding remarks are broken down into three key sections: 1) conclusions relevant to the Mataketake Region, 2) those relevant to metal enrichment, and 3) suggestions for future research.

Section 1: Conclusions relevant to the formation of the Mataketake Pegmatites

- Application of Titanium-in-biotite empirical geothermometer of Henry et al. (2005) provides further temperature ranges for the Alpine Schist (1.AS) and Mataketake Pegmatite (1(B)MP) (Figures 6.2 & 6.3). Calculated temperatures ranged from 483°C to 635°C for 1.AS, and 539°C to 614°C for 1(B)MP. These calculations provide a minimum temperature that the pegmatite must have reached at 539°C.
- In common with existing thermometry, we propose a temperature range of 539-635°C for the melting of the Alpine Schist to form the Mataketake Pegmatites (Section 6.1.2). This restricts melting reactions that exceed this temperature, notably biotite melting, which has a lower temperature bound of 740°C (Kunz et al., 2022).
- Petrological observations, and SEM analyses revealed no K-feldspar in analysed specimens of the Alpine Schist and Mataketake Pegmatites. This lack of K-feldspar in the Mataketake Pegmatites highlights heterogeneity in the Alpine Schists and Mataketake Pegmatites and contrasts with other studies (Briggs & Cottle, 2018; Pitcairn, 2004; Wallace, 1974). It also points to reduced K-feldspar involvement in melting processes and reactions, which restricts possible melting reactions inferred by this study.
- The lack of K-feldspar in 1(B)MP of this study is indicative of fluid-present melting. This is because in fluid-absent melting of muscovite, K-feldspar is produced as a reaction product (Dyck et al., 2020). However, although it can be a product in fluid-present scenarios (generated due to melt crystallisation), it is not always the case (Dyck et al., 2020). Hence, K-feldspar absence indicates fluid-present melting.
- Changes in modal abundance of phases between the Alpine Schist and Mataketake Pegmatite indicate that a greater proportion of plagioclase has contributed to the melt than mica (Section 6.1.1.1). During fluid-present muscovite melting, plagioclase is more intensely consumed than muscovite, because the solidus of quartz + plagioclase is suppressed with increasing H₂O activity, while muscovite remains stable (Patiño Douce & Harris, 1998; Scaillet & Pichavant, 2024). This suggests fluid-present muscovite melting within the study region (Section 6.1.1.1).
- Plagioclase is generally Sr-enriched and Rb-poor, whereas micas are Rb-enriched and Sr-poor (Section 6.1.1.2; (Inger & Harris, 1993; Weinberg & Hasalová, 2015)). This results in fluid-absent mica-dehydration reactions producing melt with high Rb/Sr ratios, whilst fluid-fluxed melting produces melt with low Rb/Sr ratios (Section 6.1.1.2). This links back to the quartz + plagioclase solidus being more intensely reduced than that of muscovite (see point above).

Our study shows a reduction in calculated whole rock Rb/Sr from the Alpine Schist to the Mataketake Pegmatite (Figure 6.1), consistent with data on the region from Briggs and Cottle (2018). These data also indicate H₂O-present muscovite dehydration melting (Briggs and Cottle (2018)).

- Normative Ab-An-Or compositions shift toward more albitic compositions in the Mataketake Pegmatite relative to the schist (Section 6.1.3.1 (Figure 6.5)). This is suggestive of H₂O-present melting (Section 6.1.3.1).
- Modelling of the major elements K, Fe and Mg (KFM) indicates that at least 2.7wt% K₂O, 1.97wt% FeO and 0.84 wt% MgO was contained in the melt. As the principal hosts of KFM in this case study, mica melting is vital for satisfying this system, in particular K₂O. However, as temperature constraints negate the possibility for biotite breakdown, we include accessory phases to satisfy Fe and Mg.
- Trace element modelling (Sr, Pb, Ba and La) points to a quartz + plagioclase dominated melt, with lesser muscovite in the melting fraction (Section 6.1.3.2). This trace element modelling also requires the inclusion of accessory phases within the melting reaction, to provide La, which exists in notable quantities in monazite and epidote of this study (Section 5.1.2 & 6.1.3.2).
- Briggs and Cottle (2018) propose four possible melting reactions for the Mataketake Pegmatites. Our research systematically removes three of them as possibilities. We then refine the remaining fluid-present muscovite dehydration melting reaction to balance our trace element modelling (Section 6.1.3.2). Our proposed reaction (Reaction No.9):

$$\text{Ms} + \text{Qtz} + \text{Plag (Ab)} + \text{H}_2\text{O} \pm (\text{garnet}) \pm (\text{epidote}) \pm (\text{monazite}) \pm (\text{chlorite}) \pm (\text{ilmenite}) = \text{melt}.$$

Section 2: Conclusions relevant to metal enrichment

- This research serves as a natural case study to observe the behaviour of metals in pegmatite systems. Lithium is not enriched in the Mataketake Pegmatites; muscovite averages 41ppm, biotite averages 177ppm, and calculated whole rock Li contents are ~21.5ppm (Section 6.1.4). The recorded mica concentrations are in the lower-end of typical concentrations for granites, with biotite typically ranging from “hundreds of ppm” (I-type granites) to 2000ppm (S-type granites) (Gardiner et al., 2024). Calculated whole rock Li concentrations are significantly depleted, with sedimentary rocks, which are typically more depleted than pegmatites, averaging 125.5ppm globally (Koopmans et al., 2023). As the most Li-enriched phase in this

case study, biotite is therefore very important for sequestering and liberating Li during crustal anatexis (Section 6.2). This aligns with recent literature (Koopmans et al., 2023; Kunz et al., 2022).

- Melting of mica minerals, particularly biotite, has been shown to be crucial for enrichment of metals (e.g., Li, Sn) (Koopmans et al., 2023; Kunz et al., 2022). The depletion of whole rock Li contents from the Alpine Schist (34.7ppm) to the Mataketake Pegmatite (21.5ppm), therefore supports our proposal that biotite melting has not occurred. This is also in agreement with our temperature constraints, which remove the possibility for biotite melting (Section 6.1.2).
- This case study reconsiders the petrologic modelling of Koopmans et al. (2023) (Section 6.2 Figure 6.6)). Our analysis is discrepant from that of Koopmans et al. (2023), as we observe a depletion in Li abundance from the schist to the pegmatite. We attribute this depletion to a lack of mica melting, particularly biotite in our low-temperature, fluid-fluxed melting scenario (Section 6.2). Therefore, we refine the proposal of Koopmans et al. (2023), to recognise the importance of higher-temperature melting, particularly fluid-absent melting, to facilitate the breakdown of biotite and release of Li into the melt (see Section 6.2). In conclusion, this case study communicates the importance of biotite melting to facilitate the release of metals into the melt, and consequent enrichment.
- Enrichment of V, Cs and W in the Alpine Schist relative to the Mataketake Pegmatites may be attributed to the persistence of their host phases during the proposed melting process (Wolf et al., 2018). Wolf et al. (2018) observe less disparate concentrations of these elements between melt and residua in higher-temperature melting (NB, in both low and high temperature melting, these elements are depleted in the melted rock (Figure 6.7 (Wolf et al., 2018))). Again, this indicates that enrichment of critical metals requires higher temperature melting scenarios ($\sim 800^{\circ}\text{C}$), and the breakdown of micas, particularly biotite (Section 6.2).
- To summarise, metal enrichment in pegmatites is controlled by a combination of (i) the specific melting reaction generating partial melt, which depends on temperature and water availability, (ii) the metal contents of refractory phases as well as those contributing to melting, and (iii) the rate of melt segregation (which controls the effective partition coefficients).

Section 3: Suggestions for future work

- We were unable to comment on Sn enrichment as we did not measure muscovite Sn contents, nor whole rock abundances. This therefore marks an area for future research, with opportunity

to build on previous literature (Gardiner et al., 2024; Koopmans et al., 2023; Kunz et al., 2022).

- Analysis on different sample suites is important for verifying the validity of conclusions reached in this case study. For example, the Barrovian progression in the Central Alps, and the associated fluid-present melting (Rubatto et al., 2009), mark a similar sample suite for analysis. Ti-in-zircon thermometry has confined temperatures in this suite to 620-700°C, making the proposed temperature range similar to that of this study (Rubatto et al., 2009). Future research could encompass analysis of critical metal contents in this Barrovian facies progression, and the produced crustal melt.
- One principal assumption is that these rocks are analogous to the entirety of the schist-pegmatite system, and therefore it is important that further research is done to corroborate this investigation. The necessity for more research into the themes discussed within this paper is emphasised by the lack of observed K-feldspar in any samples, as this is disparate to petrological observations in previous literature.
- We use the Ti-in-biotite empirical geothermometer of Henry et al. (2005) in this study. To validate our proposed temperatures, other methods should be used to provide temperature constraints for the Mataketake Pegmatites. Examples of other methods include: apatite saturation thermometry (Denisova, 2020), zircon-based thermometers (including Ti-in-zircon thermometry) (Siégl et al., 2018), and Fe-Ti oxide geothermometry (Ghiorso & Sack, 1991).
- Whole-rock analyses would be a useful area of research to verify our conclusions based off our calculated whole-rock abundances. As Briggs and Cottle (2018) observed a couple samples deviating from whole-rock trends in Ab-An-Or ternary diagram, and Ba v Rb/Sr plots (Figure 6.1 & 6.5), further analysis would increase certainty on conclusions from these observations.
- This thesis originally intended to analyse Li contents of micas through the progressive metamorphic grades in New Zealand's South Island. However, grain size in less-intensely metamorphosed rocks was too small to facilitate this. Future research could look at whole-rock compositions through the metamorphic sequence, as this is an important factor in contextualising the Alpine Schist protolith. The hinterlands of orogenies are synonymous with economic pegmatite deposits (Bradley et al., 2017). As such, understanding the behaviour of critical metals throughout the metamorphic sequence may facilitate better understanding of protolith compositions. Koopmans et al. (2023) highlight the importance of an enriched protolith to produce melts that are enriched in Li. This study also indicates the necessity for an enriched protolith to enable the formation of Li-ore minerals. Consequently, understanding if and how metamorphic processes affect critical metal contents, will better contextualise this case study, and provide key information in a poorly understood domain.

8 Bibliography

- Acosta-Vigil, A., London, D., & Morgan, G. B. (2006). Experiments on the kinetics of partial melting of a leucogranite at 200 MPa H₂O and 690–800°C: compositional variability of melts during the onset of H₂O-saturated crustal anatexis. *Contributions to Mineralogy and Petrology*, 151(5), 539–557. <https://doi.org/10.1007/s00410-006-0081-8>
- Adams, C. J., Bishop, D. G., & Gabites, J. E. (1985). Potassium-argon age studies of a low-grade, progressively metamorphosed greywacke sequence, Dansey Pass, South Island, New Zealand. *Journal of the Geological Society*, 142(2), 339–349. <https://doi.org/doi:10.1144/gsjgs.142.2.0339>
- Adams, C. J., Campbell, H. J., Graham, I. J., & Mortimer, N. (1998). Torlesse, Waipapa and Caples suspect terranes of New Zealand: Integrated studies of their geological history in relation to neighbouring terranes. *International Union of Geological Sciences*, 21(4), 235–240. <https://doi.org/10.18814/epiiugs/1998/v21i4/004>
- Adams, C. J., Campbell, H. J., & Griffin, W. L. (2009). Tracing the Caples Terrane through New Zealand using detrital zircon age patterns and radiogenic isotope signatures. *New Zealand Journal of Geology and Geophysics*, 52(3), 223–245. <https://doi.org/10.1080/00288300909509888>
- Adams, C. J., Campbell, H. J., & Jongens, R. (2017). Triassic age for a conglomerate clast in the Waipapa Terrane, North Island, New Zealand. *New Zealand Journal of Geology and Geophysics*, 60(4), 519–523. <https://doi.org/10.1080/00288306.2017.1369131>
- Adams, C. J., & Gabites, J. E. (1985). Age of metamorphism and uplift in the Haast Schist Group at Haast Pass, Lake Wanaka and Lake Hawea, South Island, New Zealand. *New Zealand Journal of Geology and Geophysics*, 28, 85–96.
- Adams, C. J., & Graham, I. J. (1997). Age of metamorphism of Otago Schist in eastern Otago and determination of protoliths from initial strontium isotope characteristics. *New Zealand Journal of Geology and Geophysics*, 40(3), 275–286. <https://doi.org/10.1080/00288306.1997.9514760>
- Adams, C. J., & Kelley, S. (1998). Provenance of Permian-Triassic and Ordovician metagraywacke terranes in New Zealand: Evidence from ⁴⁰Ar/³⁹Ar dating of detrital micas. *GSA Bulletin*, 110(4), 422–432. [https://doi.org/10.1130/0016-7606\(1998\)110<0422:Poptao>2.3.Co;2](https://doi.org/10.1130/0016-7606(1998)110<0422:Poptao>2.3.Co;2)
- Andrews, P. B., Bishop, D. G., Bradshaw, J. D., & Warren, G. (1974). Geology of the Lord Range, Central Southern Alps, New Zealand. *New Zealand Journal of Geology and Geophysics*, 17(2), 271–299. <https://doi.org/10.1080/00288306.1974.10430395>
- Anenburg, M., & Katzir, Y. (2014). Muscovite dehydration melting in Si-rich metapelites: Microstructural evidence from trondhjemitic migmatites, Roded, Southern Israel. *Mineralogy and Petrology*, 108, 137–152. <https://doi.org/10.1007/s00710-013-0289-z>
- Aronson, J., L. (1965). Reconnaissance rubidium—strontium geochronology of New Zealand plutonic and metamorphic rocks. *New Zealand Journal of Geology and Geophysics*, 8(3), 401–423. <https://doi.org/10.1080/00288306.1965.10426413>
- Bacon, C. R., & Druitt, T. H. (1988). Compositional evolution of the zoned calcalkaline magma chamber of Mount Mazama, Crater Lake, Oregon. *Contributions to Mineralogy and Petrology*, 98(2), 224–256. <https://doi.org/10.1007/BF00402114>
- Barnes, P. M., de Lépinay, B. M., Collot, J.-Y., Delteil, J., & Audru, J.-C. (1998). Strain partitioning in the transition area between oblique subduction and continental collision, Hikurangi margin, New Zealand. *Tectonics*, 17(4), 534–557. <https://doi.org/https://doi.org/10.1029/98TC00974>

- Barrier, A., Bischoff, A., Nicol, A., Browne, G. H., & Bassett, K. N. (2021). Relationships between volcanism and plate tectonics: A case-study from the Canterbury Basin, New Zealand. *Marine Geology*, 433, 106397. <https://doi.org/https://doi.org/10.1016/j.margeo.2020.106397>
- Barth, N. C., Toy, V. G., Langridge, R. M., & Norris, R. J. (2012). Scale dependence of oblique plate-boundary partitioning: New insights from LiDAR, central Alpine fault, New Zealand. *Lithosphere*, 4(5), 435-448. <https://doi.org/10.1130/L201.1>
- Batt, G. E., Kohn, B. P., Braun, J., McDougall, I., & Ireland, T. R. (1999). New insight into the dynamic development of the Southern Alps, New Zealand, from detailed thermochronological investigation of the Mataketake Range pegmatites. *Geological Society, London, Special Publications*, 154(1), 261-282. <https://doi.org/doi:10.1144/GSL.SP.1999.154.01.12>
- Bea, F. (1996). Controls on the trace element composition of crustal melts. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, 87(1-2), 33-41. <https://doi.org/10.1017/S0263593300006453>
- Bea, F., Pereira, M. D., & Stroh, A. (1994). Mineral/leucosome trace-element partitioning in a peraluminous migmatite (a laser ablation-ICP-MS study). *Chemical Geology*, 117(1), 291-312. [https://doi.org/https://doi.org/10.1016/0009-2541\(94\)90133-3](https://doi.org/https://doi.org/10.1016/0009-2541(94)90133-3)
- Beard, J. S., & Lofgren, G. E. (1991). Dehydration Melting and Water-Saturated Melting of Basaltic and Andesitic Greenstones and Amphibolites at 1, 3, and 6. 9 kb. *Journal of Petrology*, 32(2), 365-401. <https://doi.org/10.1093/petrology/32.2.365>
- Beard, J. S., Lofgren, G. E., Sinha, A. K., & Tollo, R. P. (1994). Partial melting of apatite-bearing charnockite, granulite, and diorite: Melt compositions, restite mineralogy, and petrologic implications. *Journal of Geophysical Research: Solid Earth*, 99(B11), 21591-21603. <https://doi.org/https://doi.org/10.1029/94JB02060>
- Berman, R. G., Aranovich, L. Y., & Pattison, D. R. M. (1995). Reassessment of the garnet-clinopyroxene Fe-Mg exchange thermometer: II. Thermodynamic analysis. *Contributions to Mineralogy and Petrology*, 119(1), 30-42. <https://doi.org/10.1007/BF00310715>
- Beyssac, O., Cox, S. C., Vry, J., & Herman, F. (2016). Peak metamorphic temperature and thermal history of the Southern Alps (New Zealand). *Tectonophysics*, 676, 229-249. <https://doi.org/https://doi.org/10.1016/j.tecto.2015.12.024>
- Beyssac, O., Goffé, B., Chopin, C., & Rouzaud, J. N. (2002). Raman spectra of carbonaceous material in metasediments: a new geothermometer. *Journal of Metamorphic Geology*, 20(9), 859-871. <https://doi.org/https://doi.org/10.1046/j.1525-1314.2002.00408.x>
- Black, P. M., Clark, A. S. B., & Hawke, A. A. (1993). Diagenesis and very low-grade metamorphism of volcanoclastic sandstones from contrasting geodynamic environments, North Island, New Zealand: the Murihiku and Waipapa terranes. *Journal of Metamorphic Geology*, 11(3), 429-435. <https://doi.org/https://doi.org/10.1111/j.1525-1314.1993.tb00159.x>
- Blundy, J., D., & Wood, B., J. . (1991). Crystal-chemical controls on the partitioning of Sr and Ba between plagioclase feldspar, silicate melts, and hydrothermal solutions. *Geochimica et Cosmochimica Acta*, 55(1), 193-209. [https://doi.org/https://doi.org/10.1016/0016-7037\(91\)90411-W](https://doi.org/https://doi.org/10.1016/0016-7037(91)90411-W)
- Bourdelle, F., Parra, T., Chopin, C., & Beyssac, O. (2013). A new chlorite geothermometer for diagenetic to low-grade metamorphic conditions. *Contributions to Mineralogy and Petrology*, 165(4), 723-735. <https://doi.org/10.1007/s00410-012-0832-7>

- Bradley, D., & McCauley, A. (2013). A preliminary deposit model for lithium-cesium-tantalum (LCT) pegmatites (ver. 1.1, December 2016). U.S. Geological Survey Open-File Report 2013–1008. <https://doi.org/https://doi.org/10.3133/ofr20131008>
- Bradley, D., McCauley, A. D., & Stillings, L. L. (2017). Mineral-deposit model for lithium-cesium-tantalum pegmatites [Report](2010-50700). (Scientific Investigations Report, Issue. U. S. G. Survey. <https://pubs.usgs.gov/publication/sir201050700>
- Bradshaw, J. D. (1989). Cretaceous geotectonic patterns in the New Zealand Region. *Tectonics*, 8(4), 803-820. <https://doi.org/https://doi.org/10.1029/TC008i004p00803>
- Brearley, A. J., & Rubie, D. C. (1990). Effects of H₂O on the Disequilibrium Breakdown of Muscovite+Quartz. *Journal of Petrology*, 31(4), 925-956. <https://doi.org/10.1093/petrology/31.4.925>
- Breiter, K., Galiova, M., Hložková, M., Korbelová, Z., Kynický, J., & Costi, H. T. (2023). Trace element composition of micas from rare-metal granites of different geochemical affiliations. *Lithos*, 446-447, 107135. <https://doi.org/https://doi.org/10.1016/j.lithos.2023.107135>
- Briggs, S. I., & Cottle, J. M. (2018). Accessory mineral petrochronology reveals 30 m.y. of partial melting during the separation of Zealandia from eastern Gondwana. *Lithosphere*, 11(1), 169-189. <https://doi.org/10.1130/11021.1>
- Briggs, S. I., Cottle, J. M., & Smit, M. A. (2018). Record of plate boundary metamorphism during Gondwana breakup from Lu–Hf garnet geochronology of the Alpine Schist, New Zealand. *Journal of Metamorphic Geology*, 36(7), 821-841. <https://doi.org/https://doi.org/10.1111/jmg.12313>
- Campbell, H. J., & Owen, S. R. (2003). The Nelsonian Stage: A new Early Triassic local stage for New Zealand. *Journal of the Royal Society of New Zealand*, 33(1), 97--108. <https://doi.org/10.1080/03014223.2003.9517723>
- Cande, S. C., & Stock, J. M. (2004). Pacific—Antarctic—Australia motion and the formation of the Macquarie Plate. *Geophysical Journal International*, 157(1), 399-414. <https://doi.org/10.1111/j.1365-246X.2004.02224.x>
- Carroll, M., & Wyllie, P. (1990). The system tonalite-H₂O at 15 kbar and the genesis of calc-alkaline magmas. *American Mineralogist*, 75, 345-357.
- Castro, A., Guillermo Corretge, L., El-Biad, M., El-Hmidi, H., Fernandez, C., & Patino Douce, A. E. (2000). Experimental Constraints on Hercynian Anatexis in the Iberian Massif, Spain. *Journal of Petrology*, 41(10), 1471-1488. <https://doi.org/10.1093/petrology/41.10.1471>
- Černý, Peter, Blevin, P. L., Cuney, M., London, D., Hedenquist, J. W., Thompson, J. F. H., Goldfarb, R. J., & Richards, J. P. (2005). Granite-Related Ore Deposits. In *One Hundredth Anniversary Volume* (pp. 0). Society of Economic Geologists. <https://doi.org/10.5382/av100.12>
- Černý, P. (1990). Distribution, affiliation and derivation of rare-element granitic pegmatites in the Canadian Shield. *Geologische Rundschau*, 79(2), 183-226. <https://doi.org/10.1007/BF01830621>
- Černý, P. (1991). Fertile granites of Precambrian rare-element pegmatite fields: is geochemistry controlled by tectonic setting or source lithologies? *Precambrian Research*, 51(1), 429-468. [https://doi.org/https://doi.org/10.1016/0301-9268\(91\)90111-M](https://doi.org/https://doi.org/10.1016/0301-9268(91)90111-M)
- Černý, P., & Ercit, T. S. (2005). The Classification of Granitic Pegmatites Revisited. *The Canadian Mineralogist*, 43, 2005-2026. <https://doi.org/10.2113/gscanmin.43.6.2005>
- Černý, P., London, D., & Novák, M. (2012). Granitic Pegmatites as Reflections of Their Sources. *Elements*, 8(4), 289-294. <https://doi.org/10.2113/gselements.8.4.289>

- Cerny, P., Meintzer, R. E., & Anderson, A. J. (1985). Extreme fractionation in rare-element granitic pegmatites; selected examples of data and mechanisms. *The Canadian Mineralogist*, 23(3), 381-421.
- Chamberlain, C. P., K. Zeitler, P., & Cooper, A. F. (1995). Geochronologic constraints of the uplift and metamorphism along the Alpine Fault, South Island, New Zealand. *New Zealand Journal of Geology and Geophysics*, 38(4), 515--523. <https://doi.org/10.1080/00288306.1995.9514678>
- Chen, G.-N., & Grapes, R. (2007). Material and element cycling of the continental crust and summary, bookTitle= Granite Genesis: In Situ Melting and Crustal Evolution. Springer Netherlands. https://doi.org/10.1007/978-1-4020-5891-2_9
- Chen, P., Ilton, E., S., Wang, Z., Rosso, K., M., & Zhang, X. (2024). Global rare earth element resources: A concise review. *Applied Geochemistry*, 175, 106158. <https://doi.org/https://doi.org/10.1016/j.apgeochem.2024.106158>
- Clemens, J., D., Stevens, G., & Bryan, S., E. (2020). Conditions during the formation of granitic magmas by crustal melting – Hot or cold; drenched, damp or dry? *Earth-Science Reviews*, 200, 102982. <https://doi.org/https://doi.org/10.1016/j.earscirev.2019.102982>
- Collett, C. M., Duvall, A. R., Flowers, R. M., Tucker, G. E., & Upton, P. (2019). The Timing and Style of Oblique Deformation Within New Zealand's Kaikōura Ranges and Marlborough Fault System Based on Low-Temperature Thermochronology. *Tectonics*, 38(4), 1250-1272. <https://doi.org/https://doi.org/10.1029/2018TC005268>
- Conrad, W. K., Nicholls, I. A., & Wall, V. J. (1988). Water-Saturated and -Undersaturated Melting of Metaluminous and Peraluminous Crustal Compositions at 10 kb: Evidence for the Origin of Silicic Magmas in the Taupo Volcanic Zone, New Zealand, and Other Occurrences. *Journal of Petrology*, 29(4), 765-803. <https://doi.org/10.1093/petrology/29.4.765>
- Coombs, D., Landis, C., Norris, R., Sinton, J., Borns, D., & Craw, D. (1976). The Dun Mountain ophiolite belt, New Zealand, its tectonic setting, constitution, and origin, with special reference to the southern portion. *American Journal of Science*, 276, 561-603. <https://doi.org/10.2475/ajs.276.5.561>
- Cooper, A. F., & Ireland, T. R. (2015). The Pounamu terrane, a new Cretaceous exotic terrane within the Alpine Schist, New Zealand; tectonically emplaced, deformed and metamorphosed during collision of the LIP Hikurangi Plateau with Zealandia. *Gondwana Research*, 27(3), 1255-1269. <https://doi.org/https://doi.org/10.1016/j.gr.2013.11.011>
- Cooper, A. F. (1974). Multiphase deformation and its relationship to metamorphic crystallisation at Haast River, South Westland, New Zealand. *New Zealand Journal of Geology and Geophysics*, 17(4), 855--880. <https://doi.org/10.1080/00288306.1974.10418230>
- Cooper, A. F., Barreiro, B. A., Kimbrough, D. L., & Mattinson, J. M. (1987). Lamprophyre dike intrusion and the age of the Alpine fault, New Zealand. *Geology*, 15(10), 941-944. [https://doi.org/10.1130/0091-7613\(1987\)15<941:Ldiata>2.0.Co;2](https://doi.org/10.1130/0091-7613(1987)15<941:Ldiata>2.0.Co;2)
- Cooper, A. F., & Ireland, T. R. (2013). Cretaceous sedimentation and metamorphism of the western Alpine Schist protoliths associated with the Pounamu Ultramafic Belt, Westland, New Zealand. *New Zealand Journal of Geology and Geophysics*, 56(4), 188--199. <https://doi.org/10.1080/00288306.2013.809776>
- Cooper, A. F., & Palin, J. M. (2018). Two-sided accretion and polyphase metamorphism in the Haast Schist belt, New Zealand: Constraints from detrital zircon geochronology. *GSA Bulletin*, 130(9-10), 1501-1518. <https://doi.org/10.1130/b31826.1>

Craw, D., Koons, P., Horton, T., & Chamberlain, C. (2002). Tectonically Driven Fluid Flow and Gold Mineralisation in Active Collisional Orogenic Belts: Comparison between New Zealand and Western Himalaya. *Tectonophysics*, 135-153. [https://doi.org/10.1016/S0040-1951\(01\)00253-0](https://doi.org/10.1016/S0040-1951(01)00253-0)

Deer, W. A., FRS, Howie, R. A., & Zussman, J. (2013). *An Introduction to the Rock-Forming Minerals*. Mineralogical Society of Great Britain and Ireland. <https://doi.org/10.1180/dhz>

Denisova, Y. V. (2020). Apatite Saturation Thermometry of the Kozhim Granite Massif (the Subpolar Urals) Minerals: Structure, Properties, Methods of Investigation,

Duuring, P. (2020). Rare-Element Pegmatites: A Mineral Systems Analysis. <https://doi.org/10.13140/RG.2.2.35634.84166>

Dyck, B., Waters, D. J., St-Onge, M. R., & Searle, M. P. (2020). Muscovite dehydration melting: Reaction mechanisms, microstructures, and implications for anatexis. *Journal of Metamorphic Geology*, 38(1), 29-52. <https://doi.org/https://doi.org/10.1111/jmg.12511>

Ebadi, A., & Johannes, W. (1991). Beginning of melting and composition of first melts in the system Qz-Ab-Or-H₂O-CO₂. *Contributions to Mineralogy and Petrology*, 106, 286-295.

Ercit, T. S. (2005). *REE-Enriched Granitic Pegmatites (Vol. 17)*.

Ewart, A., & Griffin, W. L. (1994). Application of proton-microprobe data to trace-element partitioning in volcanic rocks. *Chemical Geology*, 117(1), 251-284. [https://doi.org/https://doi.org/10.1016/0009-2541\(94\)90131-7](https://doi.org/https://doi.org/10.1016/0009-2541(94)90131-7)

Feng, Y., Deng, C., Xiao, B., Gong, L., Yin, R., & Sun, D. (2021). Biotite geochemistry and its implication on the temporal and spatial difference of Cu and Mo mineralization at the Xiaokele porphyry Cu-Mo deposit, NE China. *Ore Geology Reviews*, 139, 104508. <https://doi.org/https://doi.org/10.1016/j.oregeorev.2021.104508>

Fischer, R. P. (1973). United States mineral resources [Report](820). (Professional Paper, Issue. U. S. G. P. Office. <https://pubs.usgs.gov/publication/pp820>

Fleming, C. A. (1969). The Mesozoic of New Zealand: Chapters in the history of the Circum-Pacific Mobile Belt. *Quarterly Journal of the Geological Society of London*, 125(1-4), 125-170. <https://doi.org/doi:10.1144/gsjgs.125.1.0125>

Fornelli, A., Piccarreta, G., Del Moro, A., & Acquafredda, P. (2002). Multi-stage melting in the lower crust of the Serre (southern Italy) [Article]. *Journal of Petrology*, 43(12), 2191-2217. <https://doi.org/10.1093/petrology/43.12.2191>

Gao, M., Xiong, X., Huang, F., Wang, J., & Wei, C. (2023). Key Factors Controlling Biotite–Silicate Melt Nb and Ta Partitioning: Implications for Nb–Ta Enrichment and Fractionation in Granites. *Journal of Geophysical Research: Solid Earth*, 128(7), e2022JB025889. <https://doi.org/https://doi.org/10.1029/2022JB025889>

Gardien, V., Thompson, A. B., Grujic, D., & Ulmer, P. (1995). Experimental melting of biotite + plagioclase + quartz ± muscovite assemblages and implications for crustal melting. *Journal of Geophysical Research: Solid Earth*, 100(B8), 15581-15591. <https://doi.org/https://doi.org/10.1029/95JB00916>

Gardien, V., Thompson, A. B., & Ulmer, P. (2000). Melting of Biotite + Plagioclase + Quartz Gneisses: the Role of H₂O in the Stability of Amphibole. *Journal of Petrology*, 41(5), 651-666. <https://doi.org/10.1093/petrology/41.5.651>

Gardiner, N., J., Palin, R., M., Koopmans, L., Mangler, M., F., & Robb, L., J. (2024). On tin and lithium granite systems: A crustal evolution perspective. *Earth-Science Reviews*, 258, 104947. <https://doi.org/https://doi.org/10.1016/j.earscirev.2024.104947>

Genier, F., Bussy, F., Epard, J.-L., & Baumgartner, L. (2008). Water-assisted migmatization of metagraywackes in a Variscan shear zone, Aiguilles-Rouges massif, western Alps. *Lithos*, 102(3), 575-597. <https://doi.org/https://doi.org/10.1016/j.lithos.2007.07.024>

Ghiorso, M. S., & Sack, O. (1991). Fe-Ti oxide geothermometry: thermodynamic formulation and the estimation of intensive variables in silicic magmas. *Contributions to Mineralogy and Petrology*, 108(4), 485-510. <https://doi.org/https://doi.org/10.1007/BF00303452>

Ginsburg, A., Timofeyev, I., & Feldman, L. (1979). Principles of geology of the granitic pegmatites. Nedra, Moscow, 296.

Graham, I. J., & Mortimer, N. (1992). Terrane characterisation and timing of metamorphism in the Otago Schist, New Zealand, using Rb-Sr and K-Ar geochronology. *New Zealand Journal of Geology and Geophysics*, 35(4), 391-401. <https://doi.org/https://doi.org/10.1080/00288306.1992.9514534>

Grapes, R., H. . (1995). Uplift and exhumation of Alpine Schist, Southern Alps, New Zealand: Thermobarometric constraints. *New Zealand Journal of Geology and Geophysics*, 38(4), 525--533. <https://doi.org/https://doi.org/10.1080/00288306.1995.9514679>

Grapes, R., & Otsuki, M. (1983). Peristerite compositions in quartzofeldspathic schists, Franz Josef-Fox Glacier Area, New Zealand. *Journal of Metamorphic Geology*, 1(1), 47-61. <https://doi.org/https://doi.org/10.1111/j.1525-1314.1983.tb00264.x>

Grapes, R., & Watanabe, T. (1992). Metamorphism and uplift of Alpine schist in the Franz Josef-Fox Glacier area of the Southern Alps, New Zealand. *Journal of Metamorphic Geology*, 10(2), 171-180. <https://doi.org/https://doi.org/10.1111/j.1525-1314.1992.tb00077.x>

Grapes, R. H., & Watanabe, T. (1994). Mineral composition variation in Alpine Schist, Southern Alps, New Zealand: Implications for recrystallization and exhumation. *Island Arc*, 3(3), 163-181. <https://doi.org/https://doi.org/10.1111/j.1440-1738.1994.tb00105.x>

Gray, D. R., & Foster, D. A. (2004). ⁴⁰Ar/³⁹Ar thermochronologic constraints on deformation, metamorphism and cooling/exhumation of a Mesozoic accretionary wedge, Otago Schist, New Zealand. *Tectonophysics*, 385(1), 181-210. <https://doi.org/https://doi.org/10.1016/j.tecto.2004.05.001>

Grindley, G. W. (1963). Structure of the alpine schists of South Westland, Southern Alps, New Zealand. *New Zealand Journal of Geology and Geophysics*, 6(5), 872--930. <https://doi.org/https://doi.org/10.1080/00288306.1963.10423630>

Heinrich, E., WM., & Levinson, A. A. (1955). Studies in the Mica Group; Mangan-Muscovite from Mattkarr, Finland. *American Mineralogist*, 40(11-12), 1132-1134.

Henry, D. J., & Guidotti, C. V. (2002). Titanium in biotite from metapelitic rocks: Temperature effects, crystal-chemical controls, and petrologic applications. *American Mineralogist*, 87(4), 375-382. <https://doi.org/doi:10.2138/am-2002-0401>

Henry, D. J., Guidotti, C. V., & Thomson, J. A. (2005). The Ti-saturation surface for low-to-medium pressure metapelitic biotites: Implications for geothermometry and Ti-substitution mechanisms [Article]. *American Mineralogist*, 90(2-3), 316-328. <https://doi.org/https://doi.org/10.2138/am.2005.1498>

- Hodges, K. V., & Bowring, S. A. (1995). $^{40}\text{Ar}/^{39}\text{Ar}$ thermochronology of isotopically zoned micas: Insights from the southwestern USA proterozoic orogen. *Geochimica et Cosmochimica Acta*, 59(15), 3205-3220. [https://doi.org/https://doi.org/10.1016/0016-7037\(95\)00209-I](https://doi.org/https://doi.org/10.1016/0016-7037(95)00209-I)
- Holm, D. K., Norris, R. J., & Craw, D. (1989). Brittle and ductile deformation in a zone of rapid uplift: Central Southern Alps, New Zealand. *Tectonics*, 8(2), 153-168. <https://doi.org/https://doi.org/10.1029/TC008i002p00153>
- Holness, M. (2018). Melt segregation from silicic crystal mushes: a critical appraisal of possible mechanisms and their microstructural record. *Contributions to Mineralogy and Petrology*, 173. <https://doi.org/10.1007/s00410-018-1465-2>
- Holness, M. B., & Clemens, J. D. (1999). Partial melting of the Appin Quartzite driven by fracture-controlled H₂O infiltration in the aureole of the Ballachulish Igneous Complex, Scottish Highlands. *Contributions to Mineralogy and Petrology*, 136(1), 154-168. <https://doi.org/10.1007/s004100050529>
- Holness, M. B., & Isherwood, C. E. (2003). The aureole of the Rum Tertiary Igneous Complex, Scotland. *Journal of the Geological Society*, 160(1), 15-27. <https://doi.org/10.1144/0016-764901-098>
- Holness, M. B., & Sawyer, E. W. (2008). On the Pseudomorphing of Melt-filled Pores During the Crystallization of Migmatites. *Journal of Petrology*, 49(7), 1343-1363. <https://doi.org/10.1093/petrology/egn028>
- Holtz, F., & Johannes, W. (1991). Genesis of Peraluminous Granites I. Experimental Investigation of Melt Compositions at 3 and 5 kb and Various H₂O Activities. *Journal of Petrology*, 32(5), 935-958. <https://doi.org/10.1093/petrology/32.5.935>
- Icenhower, J., & London, D. (1995). An experimental study of element partitioning among biotite, muscovite, and coexisting peraluminous silicic melt at 200 MPa (H₂O). 1995, *American Mineralogist*, 1229-1251. <https://doi.org/10.2138/am-1995-11-1213>
- Imai, N., Lee, H. K., & Machida, M. (1980). Vanadium-Bearing Green Mica from the Jangsan Quartzite in the Janggun Mine Area, Republic of Korea. *Clay Science*, 5(5), 221-236. <https://doi.org/10.11362/jcssjclayscience1960.5.221>
- Inger, S., & Harris, N. (1993). Geochemical Constraints on Leucogranite Magmatism in the Langtang Valley, Nepal Himalaya. *Journal of Petrology*, 34(2), 345-368. <https://doi.org/10.1093/petrology/34.2.345>
- Ireland, T., R. . (1992). Crustal evolution of New Zealand: Evidence from age distributions of detrital zircons in Western Province paragneisses and Torlesse greywacke. *Geochimica et Cosmochimica Acta*, 56(3), 911-920. [https://doi.org/https://doi.org/10.1016/0016-7037\(92\)90036-I](https://doi.org/https://doi.org/10.1016/0016-7037(92)90036-I)
- Jamieson, R. A., Unsworth, M. J., Harris, N. B. W., Rosenberg, C. L., & Schulmann, K. (2011). Crustal Melting and the Flow of Mountains. *Elements*, 7(4), 253-260. <https://doi.org/10.2113/gselements.7.4.253>
- Johnson, T., Yakymchuk, C., & Brown, M. (2021). Crustal melting and suprasolidus phase equilibria: From first principles to the state-of-the-art. *Earth-Science Reviews*, 221, 103778. <https://doi.org/https://doi.org/10.1016/j.earscirev.2021.103778>
- Johnson, T. E., Gibson, R. L., Brown, M., Buick, I. S., & Cartwright, I. (2003). Partial melting of metapelitic rocks beneath the Bushveld Complex, South Africa [Article]. *Journal of Petrology*, 44(5), 789-813. <https://doi.org/10.1093/petrology/44.5.789>

- Kamp, P. J. J., Green, P. F., & White, S. H. (1989). Fission track analysis reveals character of collisional tectonics in New Zealand. *Tectonics*, 8(2), 169-195.
<https://doi.org/https://doi.org/10.1029/TC008i002p00169>
- Kelley, K. D., Scott, C., Polyak, D. E., & Kimball, B. E. (2017). Vanadium [Report](1802U). (Professional Paper, Issue. U. S. G. Survey. <https://pubs.usgs.gov/publication/pp1802U>
- King, P., R. . (2000). Tectonic reconstructions of New Zealand: 40 Ma to the Present. *New Zealand Journal of Geology and Geophysics*, 43(4), 611--638.
<https://doi.org/10.1080/00288306.2000.9514913>
- Klemme, S., Günther, D., Hametner, K., Prowatke, S., & Zack, T. (2006). The partitioning of trace elements between ilmenite, ulvospinel, armalcolite and silicate melts with implications for the early differentiation of the moon. *Chemical Geology*, 234(3), 251-263.
<https://doi.org/https://doi.org/10.1016/j.chemgeo.2006.05.005>
- Knoll, T., Huet, B., Schuster, R., Mali, H., Ntaflos, T., & Hauzenberger, C. (2023). Lithium pegmatite of anatectic origin – A case study from the Austroalpine Unit Pegmatite Province (Eastern European Alps): Geological data and geochemical modeling. *Ore Geology Reviews*, 154, 105298.
<https://doi.org/https://doi.org/10.1016/j.oregeorev.2023.105298>
- Koopmans, L., Martins, T., Linnen, R., Gardiner, N. J., Breasley, C. M., Palin, R. M., Groat, L. A., Silva, D., & Robb, L. J. (2023). The formation of lithium-rich pegmatites through multi-stage melting. *Geology*, 52(1), 7-11. <https://doi.org/10.1130/g51633.1>
- Kunz, B. E., Warren, C. J., Jenner, F. E., Harris, N. B. W., & Argles, T. W. (2022). Critical metal enrichment in crustal melts: The role of metamorphic mica. *Geology*, 50(11), 1219-1223.
<https://doi.org/10.1130/g50284.1>
- Landis, C. A. (1974). Stratigraphy, lithology, structure, and metamorphism of Permian, Triassic, and Tertiary rocks between the Mararoa River and Mount Snowdon, western Southland, New Zealand. *Journal of the Royal Society of New Zealand*, 4(3), 229--251.
<https://doi.org/10.1080/03036758.1974.10419392>
- Langridge, R. M., Ries, W. F., Farrier, T., Barth, N. C., Khajavi, N., & G.P. (2014). Developing sub 5-m LiDAR DEMs for forested sections of the Alpine and Hope faults, South Island, New Zealand: Implications for structural interpretations. *Journal of Structural Geology*, 64, 53-66.
<https://doi.org/https://doi.org/10.1016/j.jsg.2013.11.007>
- Leeman, W., P. . (1979). Partitioning of Pb between volcanic glass and coexisting sanidine and plagioclase feldspars. *Geochimica et Cosmochimica Acta*, 43(1), 171-175.
[https://doi.org/https://doi.org/10.1016/0016-7037\(79\)90056-5](https://doi.org/https://doi.org/10.1016/0016-7037(79)90056-5)
- Li, P., Li, J., Chen, Z., Liu, X., Huang, Z., & Zhou, F. (2021). Compositional evolution of the muscovite of Renli pegmatite-type rare-metal deposit, northeast Hunan, China: Implications for its petrogenesis and mineralization potential. *Ore Geology Reviews*, 138, 104380.
<https://doi.org/https://doi.org/10.1016/j.oregeorev.2021.104380>
- Lillie, A. R., Gunn, B. M., & Robinson, P. (1957). Structural observations in central Alpine Region of New Zealand. *Transaction and Proceedings of the Royal Society of New Zealand*, 85(1957-58), 113-129. <https://paperspast.natlib.govt.nz/periodicals/TPRSNZ1957-85.2.5.8>
- Lillie, A. R., & Mason, B. H. (1955). Geological reconnaissance of the district between Franz Josef Glacier and Copland Valley. *Transactions of the Royal Society of New Zealand*, 82, 237-284.

- Little, T., Cox, S., Vry, J., & Batt, G. (2005). Variations in exhumation level and uplift rate along the oblique-slip Alpine Fault, Central Southern Alps, New Zealand. *Geological Society of America Bulletin*, 117, 707. <https://doi.org/10.1130/B25500.1>
- Little, T. A., Holcombe, R. J., & Ilg, B. R. (2002). Ductile fabrics in the zone of active oblique convergence near the Alpine Fault, New Zealand: identifying the neotectonic overprint. *Journal of Structural Geology*, 24(1), 193-217. [https://doi.org/https://doi.org/10.1016/S0191-8141\(01\)00059-1](https://doi.org/https://doi.org/10.1016/S0191-8141(01)00059-1)
- Little, T. A., Mortimer, N., & McWilliams, M. (1999). An episodic Cretaceous cooling model for the Otago-Marlborough Schist, New Zealand, based on $^{40}\text{Ar}/^{39}\text{Ar}$ white mica ages. *New Zealand Journal of Geology and Geophysics*, 42(3), 305--325. <https://doi.org/10.1080/00288306.1999.9514848>
- London, D. (1984). Experimental phase equilibria in the system $\text{LiAlSiO}_4\text{--SiO}_2\text{--H}_2\text{O}$: a petrogenetic grid for lithium-rich pegmatites. *American Mineralogist*, 69(11-12), 995-1004.
- London, D. (2008). Pegmatites. *The Canadian Mineralogist*, 46(5), 1374-1375.
- Longerich, H. P., Jackson, S. E., & Günther, D. (1996). Inter-laboratory note. Laser ablation inductively coupled plasma mass spectrometric transient signal data acquisition and analyte concentration calculation [10.1039/JA9961100899]. *Journal of Analytical Atomic Spectrometry*, 11(9), 899-904. <https://doi.org/10.1039/JA9961100899>
- Lourenço, D., L. , Rozel, A., & Tackley, P., J. . (2016). Melting-induced crustal production helps plate tectonics on Earth-like planets. *Earth and Planetary Science Letters*, 439, 18-28. <https://doi.org/https://doi.org/10.1016/j.epsl.2016.01.024>
- Mackay, D. A. R., & Simandl, G. J. (2014). Geology, market and supply chain of niobium and tantalum—a review. *Mineralium Deposita*, 49(8), 1025-1047. <https://doi.org/10.1007/s00126-014-0551-2>
- Mackinnon, T. C. (1983). Origin of the Torlesse terrane and coeval rocks, South Island, New Zealand. *GSA Bulletin*, 94(8), 967-985. [https://doi.org/10.1130/0016-7606\(1983\)94<967:Oottta>2.0.Co;2](https://doi.org/10.1130/0016-7606(1983)94<967:Oottta>2.0.Co;2)
- Maneta, V., Baker, D., & Minarik, W. (2015). Evidence for lithium-aluminosilicate supersaturation of pegmatite-forming melts. *Contributions to Mineralogy and Petrology*, 170. <https://doi.org/10.1007/s00410-015-1158-z>
- Mayne, M. J., Stevens, G., & Moyen, J.-F. (2020). A phase equilibrium investigation of selected source controls on the composition of melt batches generated by sequential melting of an average metapelite. *Geological Society, London, Special Publications*, 491(1), 223-241. <https://doi.org/doi:10.1144/SP491-2018-121>
- McCarthy, T. S., & Groves, D. I. (1979). The Blue Tier Batholith, Northeastern Tasmania - A cumulate-like product of fractional crystallization [Article]. *Contributions to Mineralogy and Petrology*, 71(2), 193-209. <https://doi.org/10.1007/BF00375436>
- Menzies, C. D. (2012). Fluid Flow Associated with the Alpine Fault, South Island, New Zealand [University of Southampton].
- Michaud, J., Pichavant, M., & Villaros, A. (2021). Rare elements enrichment in crustal peraluminous magmas: insights from partial melting experiments. *Contributions to Mineralogy and Petrology*, 176. <https://doi.org/10.1007/s00410-021-01855-9>
- Mohammadi, N., Lentz, D., R. , McFarlane, C., R. M. , & Yang, X.-M. (2021). Biotite composition as a tool for exploration: An example from Sn-W-Mo-bearing Mount Douglas Granite, New Brunswick, Canada. *Lithos*, 382-383, 105926. <https://doi.org/https://doi.org/10.1016/j.lithos.2020.105926>

- Mortimer, N. (2000). Metamorphic discontinuities in orogenic belts: example of the garnet–biotite–albite zone in the Otago Schist, New Zealand. *International Journal of Earth Sciences*, 89(2), 295–306. <https://doi.org/10.1007/s005310000086>
- Mortimer, N. (2004). New Zealand's Geological Foundations. *Gondwana Research*, 7(1), 261–272. [https://doi.org/https://doi.org/10.1016/S1342-937X\(05\)70324-5](https://doi.org/https://doi.org/10.1016/S1342-937X(05)70324-5)
- Mortimer, N., & Cooper, A. F. (2004). U-Pb and Sm-Nd ages from the Alpine Schist, New Zealand. *New Zealand Journal of Geology and Geophysics*, 47(1), 21–28. <https://doi.org/10.1080/00288306.2004.9515034>
- Mortimer, N., Tulloch, A. J., Spark, R. N., Walker, N. W., Ladley, E., Allibone, A., & Kimbrough, D. L. (1999). Overview of the Median Batholith, New Zealand: a new interpretation of the geology of the Median Tectonic Zone and adjacent rocks. *Journal of African Earth Sciences*, 29(1), 257–268. [https://doi.org/https://doi.org/10.1016/S0899-5362\(99\)00095-0](https://doi.org/https://doi.org/10.1016/S0899-5362(99)00095-0)
- Murphy, D. B. (2010). Metamorphism and the P-T History of Alpine Schist from the Newton Range, Southern Alps, New Zealand. [Thesis]. Open Access Te Herenga Waka-Victoria University of Wellington. . <https://doi.org/https://doi.org/10.26686/wgtn.16984642.v1>
- Nash, W. P., & Crecraft, H. R. (1985). Partition coefficients for trace elements in silicic magmas. *Geochimica et Cosmochimica Acta*, 49(11), 2309–2322. [https://doi.org/https://doi.org/10.1016/0016-7037\(85\)90231-5](https://doi.org/https://doi.org/10.1016/0016-7037(85)90231-5)
- Nehring, F., Foley, S. F., & Hölttä, P. (2010). Trace element partitioning in the granulite facies. *Contributions to Mineralogy and Petrology*, 159(4), 493–519. <https://doi.org/10.1007/s00410-009-0437-y>
- Nielsen, R. L., Ustunisik, G., Weinsteiger, A. B., Tepley III, F. J., Johnston, A. D., & Kent, A. J. R. (2017). Trace element partitioning between plagioclase and melt: An investigation of the impact of experimental and analytical procedures. *Geochemistry, Geophysics, Geosystems*, 18(9), 3359–3384. <https://doi.org/https://doi.org/10.1002/2017GC007080>
- Norris, R., & Cooper, A. (2003). Very high strains recorded in mylonites along the Alpine Fault, New Zealand: Implications for the deep structure of plate boundary faults. *Journal of Structural Geology*, 25, 2141–2157. [https://doi.org/10.1016/S0191-8141\(03\)00045-2](https://doi.org/10.1016/S0191-8141(03)00045-2)
- Norris, R. J., & Cooper, A. F. (2001). Late Quaternary slip rates and slip partitioning on the Alpine Fault, New Zealand. *Journal of Structural Geology*, 23(2), 507–520. [https://doi.org/https://doi.org/10.1016/S0191-8141\(00\)00122-X](https://doi.org/https://doi.org/10.1016/S0191-8141(00)00122-X)
- Norris, R. J., & Cooper, A. F. (1995). Origin of small-scale segmentation and transpressional thrusting along the Alpine fault, New Zealand. *GSA Bulletin*, 107(2), 231–240. [https://doi.org/10.1130/0016-7606\(1995\)107<0231:Oosssa>2.3.Co;2](https://doi.org/10.1130/0016-7606(1995)107<0231:Oosssa>2.3.Co;2)
- Norris, R. J., & Cooper, A. F. (2007). The Alpine Fault, New Zealand: Surface Geology and Field Relationships. In *A Continental Plate Boundary: Tectonics at South Island, New Zealand* (pp. 157–175). <https://doi.org/https://doi.org/10.1029/175GM09>
- Norris, R. J., Koons, P. O., & Cooper, A. F. (1990). The obliquely-convergent plate boundary in the South Island of New Zealand: implications for ancient collision zones. *Journal of Structural Geology*, 12(5), 715–725. [https://doi.org/https://doi.org/10.1016/0191-8141\(90\)90084-C](https://doi.org/https://doi.org/10.1016/0191-8141(90)90084-C)
- Patiño Douce, A., & Johnston, A. (1991). Phase equilibria and melt productivity in the pelitic system: implications for the origin of peraluminous granitoids and aluminous granulites. *Contributions to Mineralogy and Petrology*, 107, 202–218. <https://doi.org/10.1007/BF00310707>

- Patiño Douce, A. E. (2005). Vapor-Absent Melting of Tonalite at 15–32 kbar. *Journal of Petrology*, 46(2), 275–290. <https://doi.org/10.1093/petrology/egh071>
- Patino Douce, A. E., & Beard, J. S. (1996). Effects of P, f(O₂) and Mg/Fe Ratio on Dehydration Melting of Model Metagreywackes. *Journal of Petrology*, 37(5), 999–1024. <https://doi.org/10.1093/petrology/37.5.999>
- Patiño Douce, A. E., & Beard, J. S. (1995). Dehydration-melting of Biotite Gneiss and Quartz Amphibolite from 3 to 15 kbar. *Journal of Petrology*, 36(3), 707–738. <https://doi.org/10.1093/petrology/36.3.707>
- Patiño Douce, A. E., & Harris, N. (1998). Experimental Constraints on Himalayan Anatexis. *Journal of Petrology*, 39(4), 689–710. <https://doi.org/10.1093/petroj/39.4.689>
- Paton, C., Hellstrom, J., Paul, B., Woodhead, J., & Hergt, J. (2011). Iolite: Freeware for the visualisation and processing of mass spectrometric data [10.1039/C1JA10172B]. *Journal of Analytical Atomic Spectrometry*, 26(12), 2508–2518. <https://doi.org/10.1039/C1JA10172B>
- Pattison, D. R. M. (1985). Petrogenesis of pelitic rocks in the Ballachulish thermal aureole. [PhD Thesis, University of Edinburgh]. <http://hdl.handle.net/1842/15601>
- Pattison, D. R. M. (1987). Variations in Mg/(Mg+Fe), F, and (Fe,Mg)Si=2Al in pelitic minerals in the Ballachulish thermal aureole, Scotland. *American Mineralogist*, 72, 255–272.
- Pattison, D. R. M. (1989). P-T conditions and the influence of graphite on pelitic phase relations in the Ballachulish aureole, Scotland. *Journal of Petrology*, 30, 1219–1244.
- Pattison, D. R. M. (1991). P-T-a(H₂O) conditions in the thermal aureole. In G.Voll, J. Topel, D.R.M. Pattison, and F. Seifert, Eds., *Equilibrium and kinetics in contact metamorphism: The Ballachulish Igneous Complex and its aureole*. Springer Verlag, Heidelberg.
- Pattison, D. R. M., & Harte, B. (1991). Petrography and Mineral Chemistry of Pelites , bookTitle= Equilibrium and Kinetics in Contact Metamorphism: The Ballachulish Igneous Complex and Its Aureole. Springer Berlin Heidelberg. https://doi.org/10.1007/978-3-642-76145-4_8
- Pattison, D. R. M., Spear, F. S., Debuhr, C. L., Cheney, J. T., & Guidotti, C. V. (2002). Thermodynamic modelling of the reaction muscovite+cordierite→Al₂SiO₅+biotite+quartz+H₂O: constraints from natural assemblages and implications for the metapelitic petrogenetic grid. *Journal of Metamorphic Geology*, 20(1), 99–118. <https://doi.org/https://doi.org/10.1046/j.0263-4929.2001.356.356.x>
- Peterson, J. W., Chacko, T., & Kuehner, S. M. (1991). The effects of fluorine on the vapor-absent melting of phlogopite + quartz: Implications for deep-crustal processes. *American Mineralogist*, 76(3–4), 470–476.
- Pichavant, M., Holtz, F., & McMillan, P., F. . (1992). Phase relations and compositional dependence of H₂O solubility in quartz-feldspar melts. *Chemical Geology*, 96(3), 303–319. [https://doi.org/https://doi.org/10.1016/0009-2541\(92\)90061-9](https://doi.org/https://doi.org/10.1016/0009-2541(92)90061-9)
- Pickering, J. M., & Johnston, D. A. (1998). Fluid-Absent Melting Behavior of a Two-Mica Metapelite: Experimental Constraints on the Origin of Black Hills Granite. *Journal of Petrology*, 39(10), 1787–1804. <https://doi.org/10.1093/petroj/39.10.1787>

Pitcairn, I. (2004). Sources of fluids and metals in orogenic deposits : the Otago Schists, New Zealand.

Richards, J. P. (2018). A Shake-Up in the Porphyry World? *Economic Geology*, 113(6), 1225-1233. <https://doi.org/10.5382/econgeo.2018.4589>

Ring, U., Glodny, J., Angiboust, S., Little, T., & Lang, K. A. (2019). Middle to Late Miocene Age for the End of Amphibolite-Facies Mylonitization of the Alpine Schist, New Zealand: Implications for Onset of Transpression Across the Alpine Fault. *Tectonics*, 38(12), 4335-4359. <https://doi.org/https://doi.org/10.1029/2019TC005577>

Riofrancos, T. (2025, March 12th 2025). The 'critical minerals' rush could result in a resource war. *Financial Times*. <https://www.ft.com/content/b3709429-a99b-4105-afa5-001d08a3fd80>

Robertson, A. H. F., Campbell, H. J., Johnston, M. R., & Palamakumbra, R. (2019). Chapter 15 Construction of a Paleozoic–Mesozoic accretionary orogen along the active continental margin of SE Gondwana (South Island, New Zealand): summary and overview. *Geological Society, London, Memoirs*, 49(1), 331-372. <https://doi.org/doi:10.1144/M49.8>

Romer, R., L. , & Kroner, U. (2016). Phanerozoic tin and tungsten mineralization—Tectonic controls on the distribution of enriched protoliths and heat sources for crustal melting. *Gondwana Research*, 31, 60-95. <https://doi.org/https://doi.org/10.1016/j.gr.2015.11.002>

Romer, R. L., & Kroner, U. (2015). Sediment and weathering control on the distribution of Paleozoic magmatic tin–tungsten mineralization. *Mineralium Deposita*, 50(3), 327-338. <https://doi.org/10.1007/s00126-014-0540-5>

Rong, J., & Wang, F. (2016). Metasomatic Textures in Granites. <https://doi.org/10.1007/978-981-10-0666-1>

Roser, B. P., & Korsch, R. J. (1999). Geochemical characterization, evolution and source of a Mesozoic accretionary wedge: the Torlesse terrane, New Zealand. *Geological Magazine*, 136(5), 493-512. <https://doi.org/10.1017/S0016756899003003>

Rubatto, D., Hermann, J., Berger, A., & Engi, M. (2009). Protracted fluid-induced melting during Barrovian metamorphism in the Central Alps. *Contributions to Mineralogy and Petrology*, 158(6), 703-722. <https://doi.org/10.1007/s00410-009-0406-5>

Rushmer, T. (1996). Melt segregation in the lower crust: how have experiments helped us? *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, 87(1-2), 73-83. <https://doi.org/10.1017/S0263593300006490>

Sallet, R., Price, J., Babinski, M., Moritz, R., de Souza, Z., & Chiaradia, M. (2015). Experimental Anatexis, Fluorine Geochemistry and Lead-isotope Constraints on Granite Petrogenesis in the Seridó Belt, Borborema Province, Northeastern Brazil. *Chemical Geology*, 400. <https://doi.org/10.1016/j.chemgeo.2015.02.011>

Sallet, R., Price, J., D., & Moritz, R. (2018). Natural and experimental fluorine substitution in biotite: Implications for fluid-rock thermochronometry and application to the Seridó Belt, northeastern Brazil. *Chemical Geology*, 482, 32-45. <https://doi.org/https://doi.org/10.1016/j.chemgeo.2018.01.019>

Sallet, R., Price, J. D., Ribeiro, C., Hollanda, M. H. B. M., Sayeg, I. J., & Harlov, D. (2023). Fluorine behavior during experimental muscovite dehydration melting and natural partitioning between micas: Implications for the petrogenesis of peraluminous leucogranites and pegmatites. *American Mineralogist*, 108(7), 1201-1212. <https://doi.org/10.2138/am-2022-8663>

- Sawyer, E. W. (2010). Migmatites formed by water-fluxed partial melting of a leucogranodiorite protolith: Microstructures in the residual rocks and source of the fluid. *Lithos*, 116(3), 273-286. <https://doi.org/https://doi.org/10.1016/j.lithos.2009.07.003>
- Scaillet, B., & Pichavant, M. (2024). Himalayan Leucogranites: An Experimental Petrology Perspective. *Elements*, 20(6), 388-394. <https://doi.org/10.2138/gselements.20.6.388>
- Scott, J., Auer, A., Muhling, J. R., Czertowicz, T. A., Cooper, A. F., Billia, M. A., & Kennedy, A. K. (2015). New P–T and U–Pb constraints on Alpine Schist metamorphism in south Westland, New Zealand. *New Zealand Journal of Geology and Geophysics*, 58(4), 385--397. <https://doi.org/10.1080/00288306.2015.1093005>
- Scott, J. M., Waight, T. E., van der Meer, Q. H. A., Palin, J. M., Cooper, A. F., & Münker, C. (2014). Metasomatized ancient lithospheric mantle beneath the young Zealandia microcontinent and its role in HIMU-like intraplate magmatism. *Geochemistry, Geophysics, Geosystems*, 15(9), 3477-3501. <https://doi.org/https://doi.org/10.1002/2014GC005300>
- Sheppard, D. S., Adams, C. J., & Bird, G. W. (1975). Age of Metamorphism and Uplift in the Alpine Schist Belt, New Zealand. *GSA Bulletin*, 86(8), 1147-1153. [https://doi.org/10.1130/0016-7606\(1975\)86<1147:Aomaui>2.0.Co;2](https://doi.org/10.1130/0016-7606(1975)86<1147:Aomaui>2.0.Co;2)
- Siégel, C., Bryan, S. E., Allen, C. M., & Gust, D. A. (2018). Use and abuse of zircon-based thermometers: A critical review and a recommended approach to identify antecrystic zircons. *Earth-Science Reviews*, 176, 87-116. <https://doi.org/https://doi.org/10.1016/j.earscirev.2017.08.011>
- Simons, B., Andersen Jens, C. Ø., Shail Robin, K., & Jenner Frances, E. (2017). Fractionation of Li, Be, Ga, Nb, Ta, In, Sn, Sb, W and Bi in the peraluminous Early Permian Variscan granites of the Cornubian Batholith: Precursor processes to magmatic-hydrothermal mineralisation. *Lithos*, 278-281, 491-512. <https://doi.org/https://doi.org/10.1016/j.lithos.2017.02.007>
- Simons, B., Robin, K. S., & Jens, C. Ø. A. (2016). The petrogenesis of the Early Permian Variscan granites of the Cornubian Batholith: Lower plate post-collisional peraluminous magmatism in the Rhenohercynian Zone of SW England. *Lithos*, 260, 76-94. <https://doi.org/https://doi.org/10.1016/j.lithos.2016.05.010>
- Simpson, G. D. H., Cooper, A. F., & Norris, R. J. (1994). Late Quaternary evolution of the Alpine Fault Zone at Paringa, South Westland, New Zealand. *New Zealand Journal of Geology and Geophysics*, 37(1), 49--58. <https://doi.org/10.1080/00288306.1994.9514600>
- Skjerlie, K. P., & Johnston, A. D. (1993). Fluid-Absent Melting Behavior of an F-Rich Tonalitic Gneiss at Mid-Crustal Pressures: Implications for the Generation of Anorogenic Granites. *Journal of Petrology*, 34(4), 785-815. <https://doi.org/10.1093/petrology/34.4.785>
- Skjerlie, K. P., & Johnston, A. D. (1996). Vapour-Absent Melting from 10 to 20 kbar of Crustal Rocks that Contain Multiple Hydrous Phases: Implications for Anatexis in the Deep to Very Deep Continental Crust and Active Continental Margins. *Journal of Petrology*, 37(3), 661-691. <https://doi.org/10.1093/petrology/37.3.661>
- Spear, F. S., Kohn, M. J., & Cheney, J. T. (1999). P-T paths from anatectic pelites. *Contributions to Mineralogy and Petrology*, 134(1), 17-32. <https://doi.org/10.1007/s004100050466>
- Stern, R. J. (2018). The evolution of plate tectonics. *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 376(2132), 20170406. <https://doi.org/doi:10.1098/rsta.2017.0406>

- Stern, T., Okaya, D., Kleffmann, S., Scherwath, M., Henrys, S., & Davey, F. (2007). Geophysical Exploration and Dynamics of the Alpine Fault Zone. In *A Continental Plate Boundary: Tectonics at South Island, New Zealand* (pp. 207-233). <https://doi.org/10.1029/175GM11>
- Storre, B. (1972). Dry melting of muscovite+quartz in the range $P_s=7$ kb to $P_s=20$ kb. *Contributions to Mineralogy and Petrology*, 37(1), 87-89. <https://doi.org/10.1007/BF00377309>
- Streck, M., & Grunder, A. (1997). Compositional Gradients and Gaps in High-silica Rhyolites of the Rattlesnake TuV. *J. Petrol.*, 38. <https://doi.org/10.1093/petroj/38.1.133>
- Stussi, J., & Cuney, M. (1996). Nature of Biotites from Alkaline, Calc-alkaline and Peraluminous Magmas by Abdel-Fattah M. Abdel-Rahman: A Comment. *Journal of Petrology*, 37. <https://doi.org/10.1093/petrology/37.5.1025>
- Sutherland, R. (1995). The Australia-Pacific boundary and Cenozoic plate motions in the SW Pacific: Some constraints from Geosat data. *Tectonics*, 14(4), 819-831. <https://doi.org/10.1029/95TC00930>
- Sutherland, R. (1996). Transpressional development of the Australia-Pacific boundary through southern South Island, New Zealand: Constraints from Miocene-Pliocene sediments, Waiho-1 borehole, South Westland. *New Zealand Journal of Geology and Geophysics*, 39(2), 251--264. <https://doi.org/10.1080/00288306.1996.9514709>
- Sutherland, R. (1999). Basement geology and tectonic development of the greater New Zealand region: an interpretation from regional magnetic data. *Tectonophysics*, 308(3), 341-362. [https://doi.org/10.1016/S0040-1951\(99\)00108-0](https://doi.org/10.1016/S0040-1951(99)00108-0)
- Taylor, R. G. (1979). *Developments in Economic Geology*. <https://www.sciencedirect.com/bookseries/developments-in-economic-geology/vol/11/suppl/C>
- Taylor, S. R. (1955). The origin of some New Zealand metamorphic rocks as shown by their major and trace element composition. *Geochimica et Cosmochimica Acta*, 8(4), 182-197. [https://doi.org/10.1016/0016-7037\(55\)90052-1](https://doi.org/10.1016/0016-7037(55)90052-1)
- Thompson, A. B. (1982). Dehydration melting of pelitic rocks and the generation of H₂O-undersaturated granitic liquids. *American Journal of Science*, 282, 1567-1595, Article 10. <https://doi.org/10.2475/ajs.282.10.1567>
- Tippett, J. M., & Kamp, P. J. J. (1993). Fission track analysis of the Late Cenozoic vertical kinematics of continental pacific crust, South Island, New Zealand. *Journal of Geophysical Research: Solid Earth*, 98(B9), 16119-16148. <https://doi.org/10.1029/92JB02115>
- Tischendorf, G., Förster, H. J., Gottesmann, B., & Rieder, M. (2007). True and brittle micas: Composition and solid-solution series. *Mineralogical Magazine - MINER MAG*, 71, 285-320. <https://doi.org/10.1180/minmag.2007.071.3.285>
- Tischendorf, G., Rieder, M., Förster, H. J., Gottesmann, B., & Guidotti, C. V. (2004). A new approach to subdivision and graphical presentation of potassium micas. *Mineralogical Magazine*, 68, 649-667.
- Toy, V., G., Craw, D., Cooper, A., F., & Norris, R., J. . (2010). Thermal regime in the central Alpine Fault zone, New Zealand: Constraints from microstructures, biotite chemistry and fluid inclusion data. *Tectonophysics*, 485(1), 178-192. <https://doi.org/10.1016/j.tecto.2009.12.013>
- Upton, P., Song, B. R., & Koons, P., O. . (2018). Topographic control on shallow fault structure and strain partitioning near Whataroa, New Zealand demonstrates weak Alpine Fault. *New Zealand Journal of Geology and Geophysics*, 61(1), 1--8. <https://doi.org/10.1080/00288306.2017.1397706>

USGS. (2025a). Mineral Commodity Summaries 2025.
<https://pubs.usgs.gov/periodicals/mcs2025/mcs2025.pdf>

USGS. (2025b). Tungsten Statistics and Information. USGS. Retrieved 15th March from
<https://www.usgs.gov/centers/national-minerals-information-center/tungsten-statistics-and-information>

Vernon, R. (1976). *Metamorphic Processes*. Murby (London) & Wiley (New York).

Vernon, R. (2004). *A Practical Guide to Rock Microstructure*. Cambridge University.

Vernon, R. (2018). Microstructures of Metamorphic Rocks. In R. H. Vernon (Ed.), *A Practical Guide to Rock Microstructure* (2 ed., pp. 135-227). Cambridge University Press. <https://doi.org/DOI:10.1017/9781108654609.006>

Vielzeuf, D., & Holloway, J. R. (1988). Experimental determination of the fluid-absent melting relations in the pelitic system. *Contributions to Mineralogy and Petrology*, 98(3), 257-276.
<https://doi.org/10.1007/BF00375178>

Villaros, A., & Pichavant, M. (2019). Mica-liquid trace elements partitioning and the granite-pegmatite connection: The St-Sylvestre complex (Western French Massif Central). *Chemical Geology*, 528, 119265. <https://doi.org/https://doi.org/10.1016/j.chemgeo.2019.07.040>

Viswanathan, S., Singh, Y., & Mahabaleswar, B. (2012). Geochemical behaviour of vanadium, chromium, cobalt, nickel, and copper during progressive chloritization of biotites in granites. *Journal of the Geological Society of India*, 80. <https://doi.org/10.1007/s12594-012-0147-3>

Vry, J. K., Baker, J., Maas, R., Little, T. A., Grapes, R., & Dixon, M. (2004). Zoned (Cretaceous and Cenozoic) garnet and the timing of high grade metamorphism, Southern Alps, New Zealand. *Journal of Metamorphic Geology*, 22(3), 137-157. <https://doi.org/https://doi.org/10.1111/j.1525-1314.2004.00504.x>

Walcott, R. I. (1998). Modes of oblique compression: Late Cenozoic tectonics of the south island of New Zealand. *Reviews of Geophysics*, 36(1), 1-26.
<https://doi.org/https://doi.org/10.1029/97RG03084>

Wallace, R. C. (1974). Metamorphism of the Alpine Schist, Mataketake Range, South Westland, New Zealand. *Journal of the Royal Society of New Zealand*, 4(3), 253-266.
<https://doi.org/10.1080/03036758.1974.10419393>

Waters, D. J., & Whales, C. J. (1984). Dehydration melting and the granulite transition in metapelites from southern Namaqualand, S. Africa. *Contributions to Mineralogy and Petrology*, 88(3), 269-275.
<https://doi.org/10.1007/BF00380171>

Watkins, J. M., Clemens, J. D., & Treloar, P. J. (2007). Archaean TTGs as sources of younger granitic magmas: melting of sodic metatonalites at 0.6–1.2 GPa. *Contributions to Mineralogy and Petrology*, 154(1), 91-110. <https://doi.org/10.1007/s00410-007-0181-0>

Weinberg, R. F., & Hasalová, P. (2015). Water-fluxed melting of the continental crust: A review. *Lithos*, 212-215, 158-188. <https://doi.org/https://doi.org/10.1016/j.lithos.2014.08.021>

Wellman, H. W. (1955). *The Geology Between Bruce Bay and Haast River, South Westland*. New Zealand Department of Scientific and Industrial Research.
<https://books.google.co.uk/books?id=8ETwAAAAMAAJ>

White, W. M. (2018). *Encyclopedia of geochemistry : a comprehensive reference source on the chemistry of the earth*. Springer.

- Williams, J. N., Toy, V. G., Massiot, C., McNamara, D. D., Smith, S. A. F., & Mills, S. (2018). Controls on fault zone structure and brittle fracturing in the foliated hanging wall of the Alpine Fault. *Solid Earth*, 9(2), 469-489. <https://doi.org/10.5194/se-9-469-2018>
- Wise, M. A., Curry, A. C., & Harmon, R. S. (2024). Reevaluation of the K/Rb-Li Systematics in Muscovite as a Potential Exploration Tool for Identifying Li Mineralization in Granitic Pegmatites. *Minerals*, 14(1), 117. <https://www.mdpi.com/2075-163X/14/1/117>
- Wolf, M., Romer, R., L. , Franz, L., & López-Moro, F. J. (2018). Tin in granitic melts: The role of melting temperature and protolith composition. *Lithos*, 310-311, 20-30. <https://doi.org/https://doi.org/10.1016/j.lithos.2018.04.004>
- Yetton, M., D. , & Nobes, D., C. . (1998). Recent vertical offset and near-surface structure of the Alpine Fault in Westland, New Zealand, from ground penetrating radar profiling. *New Zealand Journal of Geology and Geophysics*, 41(4), 485--492. <https://doi.org/10.1080/00288306.1998.9514825>
- Yund, R. A., Quigley, J., & Tullis, J. (1989). The effect of dislocations on bulk diffusion in feldspars during metamorphism. *Journal of Metamorphic Geology*, 7(3), 337-341. <https://doi.org/https://doi.org/10.1111/j.1525-1314.1989.tb00601.x>
- Zack, T., Kronz, A., Foley, S. F., & Rivers, T. (2002). Trace element abundances in rutiles from eclogites and associated garnet mica schists. *Chemical Geology*, 184(1), 97-122. [https://doi.org/https://doi.org/10.1016/S0009-2541\(01\)00357-6](https://doi.org/https://doi.org/10.1016/S0009-2541(01)00357-6)
- Zeng, L., Asimow, P., D. , & Saleeby, J., B. . (2005). Coupling of anatexis reactions and dissolution of accessory phases and the Sr and Nd isotope systematics of anatexis melts from a metasedimentary source. *Geochimica et Cosmochimica Acta*, 69(14), 3671-3682. <https://doi.org/https://doi.org/10.1016/j.gca.2005.02.035>