

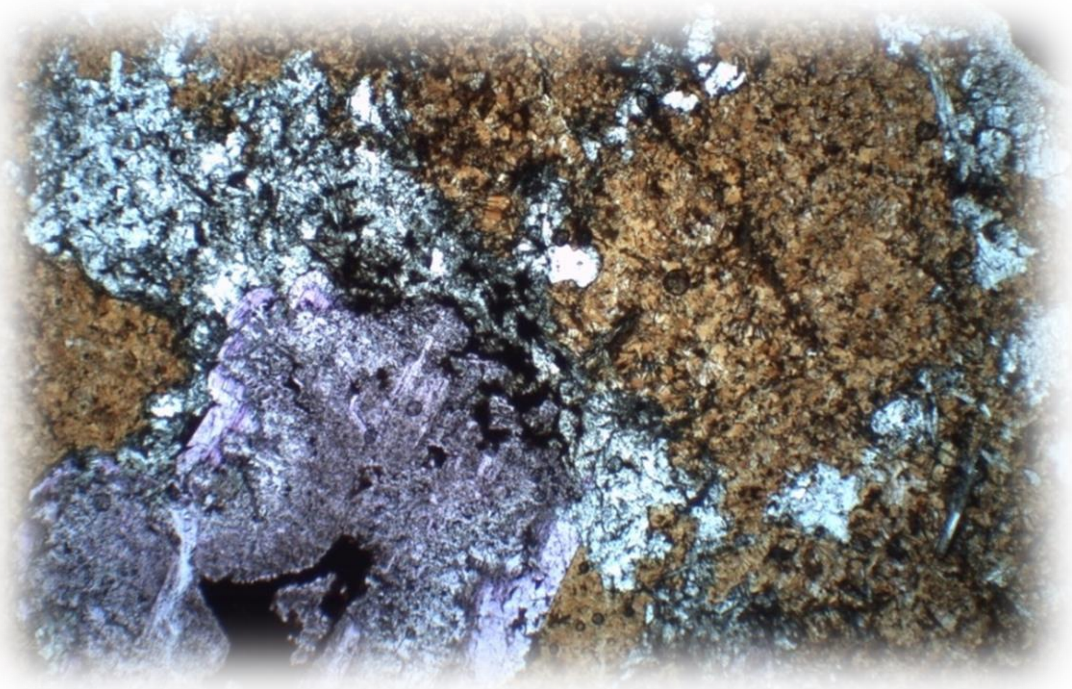
Genesis of karst-hosted manganese ores of the Postmasburg Manganese Field, South Africa with emphasis on evidence for hydrothermal processes

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Abstract

The Postmasburg Manganese Field (PMF), located in the Northern Cape Province of South Africa, once represented one of the largest sources of manganese ore worldwide. However, the discovery of the giant manganese deposits of the Kalahari Manganese Field (KMF) led to the gradual decline in manganese mining activity in the PMF. Two belts of manganese ore deposits have been distinguished in the PMF, namely the Western Belt of ferruginous manganese ores and the Eastern Belt of siliceous manganese ores. Prevailing models of ore formation in these two belts invoke karstification of manganese-rich dolomites and residual accumulation of manganese waste which later underwent diagenetic and low-grade metamorphic processes. For the most part, the role of hydrothermal processes in ore formation and metasomatic alteration is not addressed.

The identification of an abundance of common and some rare Al-, Na-, K- and Ba-bearing minerals, particularly aegirine, albite, microcline, banalsite, sérandite-pectolite, paragonite and natrolite in the PMF ores studied in this thesis, is indicative of the influence of hydrothermal activity. Enrichments in Na, K and/or Ba in the ores are generally on a percentage level for the majority of samples analysed through bulk-rock techniques. The discovery of a Ba-Mn arsenate/vanadate similar to gamagarite may also indicate that the hydrothermal fluid affecting the ores was not only alkali-rich but also probably contained some As and V. The fluid was likely to be oxidized and alkaline in nature and is thought to have been a mature basinal brine. Various replacement textures, particularly of Na- and K-rich minerals by Ba-bearing phases, suggest sequential deposition of gangue as well as ore-minerals from the hydrothermal fluid, with Ba phases being deposited at a later stage.

The stratigraphic variability of the studied ores and the deviation of their character from the pigeon-hole-type classification of ferruginous and siliceous ores in the literature, suggests that a re-evaluation of genetic models is warranted. The discovery of hydrothermally-

deposited alkali-rich assemblages in the PMF and KMF provides grounding for further investigation into a possible regional-scale hydrothermal event at least re-constituting the ores. Some shortcomings in previous works include disregard for the highly variable nature of the PMF deposits, the effects of hydrothermal activity of the ores and the existence of stratigraphic discrepancies. This study provides a single, broad model for the development of all manganese deposits of the PMF. The source of metals is attributed to all formations that stratigraphically overly the Reivilo Formation of the Campbellrand Subgroup (including the Reivilo Formation itself). The main process by which metals are accumulated is attributed to karstification of the dolomites. The interaction of oxidized, alkaline brines with the ores is considered and the overlying Asbestos Hills Subgroup BIF is suggested as a potential source of alkali metals.

Table of Contents

Chapter 1: Introduction	1
1.1. Regional Geology.....	2
1.2. The Postmasburg Manganese Field.....	8
1.2.1. Ferruginous ores of the Western Belt	8
1.2.2. Siliceous ores of the Eastern Belt	9
1.2.3. Mixed ores	10
1.3. Previous work on the genesis of PMF ores	10
1.3.1. Genesis of the Western Belt or ferruginous ores	11
1.3.2. Genesis of the Eastern Belt or siliceous ores	12
1.4. Metamorphism and Hydrothermal Activity	13
1.5. Research Aims and Objectives.....	14
Chapter 2: Sample selection, drill core logs and methods	15
2.1. Introduction	15
2.2. Diamond drill core SLT-015.....	15
2.3. Diamond drill core SLT-017.....	20
2.4. Diamond drill core SLT-018.....	21
Chapter 3: Petrography and Mineral Chemistry	22
3.1. Introduction and previous work	22
3.1.1. Eastern Belt Siliceous Ores.....	22
3.1.2. Western Belt Ferruginous Ores.....	23
3.2. Diamond Drill Core SLT-015	24
3.2.1. Summary of Analytical Methods	24
3.2.2. Clast-supported chert breccia.....	25
3.2.3. Matrix-supported, vuggy breccia	27
3.2.4. Aegirine-augite-bearing, clast-supported breccia	34
3.2.5. Aegirine-rich, matrix-supported breccia.....	36
3.2.6. Vuggy manganese ore.....	44
3.2.7. Massive ferromanganiferous ore unit	49
3.2.8. Fine-grained breccia.....	53
3.2.9. Siliceous hematite lutite and laminated ferromanganese ore.....	57

3.2.10. Summary	63
3.3. Diamond Drill Core SLT-017	64
3.4. Diamond Drill Core AKH-49.....	69
3.5. Diamond Drill Core SLT-018	72
3.6. Summary	73
Chapter 4: Bulk-Rock Geochemistry	76
4.1. General	77
4.1.1. Drill core SLT-015.....	77
4.1.2. Drill core SLT-017.....	81
4.1.3. Drill core AKH-49	82
4.1.4. Geochemical comparisons between drill cores.....	84
4.2. Trends and Correlation.....	86
4.3. Stable isotope geochemistry.....	91
4.3.1. Oxygen isotope data for braunite	91
4.3.2. Carbon and oxygen isotope data for dolomite	93
4.4. Summary	95
Chapter 5: Discussion	96
5.1. Evidence for large-scale fluid migration.....	97
5.2. Nature of hydrothermal processes.....	100
5.2.1. Fluid characteristics	100
5.2.2. Mechanisms of mineral deposition and metasomatism	104
5.3. Evaluation of existing prevalent models	108
5.4. Processes of manganese ore formation in the Postmasburg Manganese Field: an all-encompassing model.	112
5.5. Concluding Remarks.....	114
5.6. Future Research.....	115
Chapter 6: Reference List	116
Appendix I: List of Abbreviations.....	A1
Appendix II: Core logs and sample depths	A2
Appendix III: Analytical Techniques.....	A7
i. Sample Preparation	A7
ii. X-Ray Diffraction (XRD)	A7
iii. Determination of H ₂ O ⁻ and loss on ignition (LOI)	A8
iv. X-Ray Fluorescence (XRF).....	A8

v. Electron Probe Microanalysis (EPMA).....	A9
vi. Stable isotope analysis	A11
Appendix IV: EPMA Data	A12
Appendix V: XRD Data for Braunite Separates	A25

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This thesis is dedicated to my father, Cleve Fairey (1940 – 2012). He died of leukaemia during the production of this thesis. He was a good man and a good father and he is sorely missed.

Chapter 1

Introduction

Manganese is a sought-after metal in today's markets, particularly in fast-developing countries such as India and China where the steel industry is flourishing. Manganese is not only used in the steel manufacturing process but also in the battery and chemical industries (Astrup and Tsikos, 1998). This demand makes South Africa a very important stakeholder in the manganese market.

The world's single largest resource of manganese can be found in the Northern Cape Province of South Africa, predominantly in the Kalahari Manganese Field (KMF) (Astrup and Tsikos, 1998). The KMF consists of three sedimentary manganese layers hosted by the Superior-type BIF of the Hotazel Formation (Tsikos and Moore, 1997). The Postmasburg Manganese Field (PMF) also occurs in the Northern Cape Province but occurs south of the KMF. The manganese ores occur in two main belts, namely the Western and the Eastern Belts with a Mixed Type which occurs at the northern and southern extremities of the PMF (von Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). Figure 1.1 shows the study locality, drill-hole locations and the general distribution of the PMF ore types.

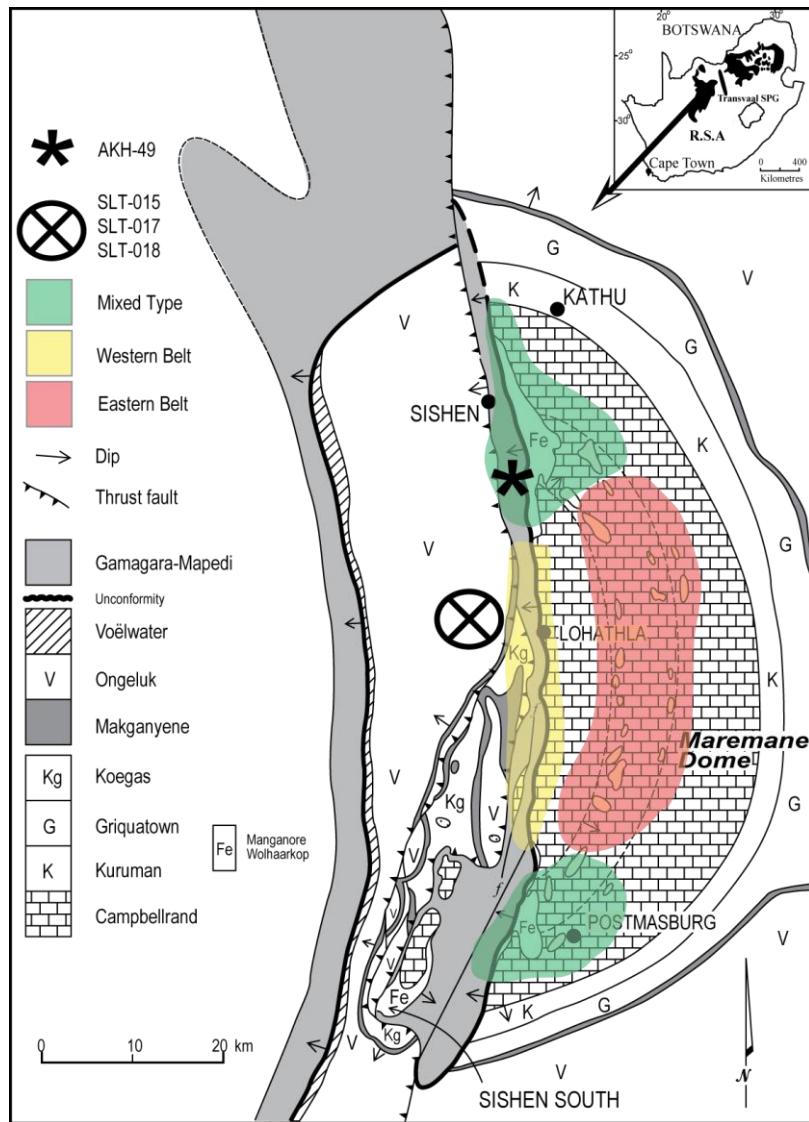


Figure 1.1: Regional geological map of the PMF area also showing the distribution of manganese mineralization and the drill core locations (Modified after Plehwe-Leisen and Klemm, 1995; Moore *et al.*, 2011).

1.1. Regional Geology

The Palaeoproterozoic Transvaal Supergroup is located in the Northern Cape Province of South Africa. Deposited over a time period of approximately 600 Ma (2.65 to 2.05 Ga), it consists of two groups, namely, the Ghaap Group and the Postmasburg Group (Table 1.1) (Tsikos *et al.*, 2003). The older Ghaap Group can be sub-divided into four subgroups. The oldest of these subgroups is the Schmidtsdrif Subgroup which comprises fluvial, shallow marine and intertidal arenites as well as platform carbonates (Beukes, 1986). This is conformably overlain by a thick (between 1500 and 1700 m) succession of carbonates known as the Campbellrand Subgroup (Beukes, 1987). According

*the drill core locations given are broad approximations. The exact location of the boreholes is sensitive information owned by Kumba Iron Ore Limited.

to Beukes (1987), the Campbellrand Subgroup consists of two main facies divided by the Griquatown fault zone: the Ghaap Plateau facies and the Prieska facies. This is clearly illustrated in Figure 1.2. The Ghaap Plateau facies is subdivided into eight formations. However, two formations in particular, namely the Reivilo Formation and the Fairfield Formation, host the manganese ores of the PMF and are also said to contribute manganese to the eventual ore bodies (von Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). The dolomitic and oolitic Monteville Formation is the lowermost formation in the Campbellrand Subgroup and is overlain by the Reivilo Formation (Altermann and Siegfried, 1997).

Table 1.1: Simplified stratigraphy of the Palaeoproterozoic Transvaal Supergroup (After Tsikos and Moore, 1997; Beukes, 1986).

		Subgroup	Formation	Predominant Lithology
Transvaal Supergroup	Postmasburg Group	Voëlwater	Moodraai	Carbonate with minor chert
			Hotazel (KMF)	Iron-formation with intercalated manganese ore
			Ongeluk	Andesitic pillow lavas
			Makganyene	Glacial diamictite
	Ghaap Group	Koegas		Mudstones and wackes
		Asbestos Hills	Griquatown	Clastic textured iron-formation
			Kuruman	Microbanded iron-formation
		Campbellrand	(PMF)	Various carbonate facies
		Schmidtsdrif		Mudstones and wackes

The Reivilo Formation predominantly consists of stromatolitic to fenestral laminated dolomites (Altermann and Siegfried, 1997) and is said to be chert-free (Gutzmer and Beukes, 1996a). The boundary between the Reivilo Formation and the overlying Fairfield Formation is defined by the development of the Kamden Member – a marker zone consisting of laminated dolomite overlain by banded iron-formation in the southern Ghaap Plateau facies (Beukes, 1987). The iron-formation pinches out toward the north with chert and ferruginous dolomite remaining (Beukes, 1987).

However, Altermann and Siegfried's (1997) work on a deep drill core through the Campbellrand dolomites near Kathu revealed that the Kamden Member can be absent all together. The overlying, chert-bearing Fairfield Formation consists of flat pebble conglomerates and dolmicrites (Altermann and Siegfried, 1997) with the upper boundary defined by a dolomite-clast breccia with a shale matrix (Beukes, 1987). This breccia signifies the base of the Klipfontein Heuwel Formation which consists of markedly silicified stromatolitic dolomites as well as chert beds (Altermann and Siegfried, 1997). The Papkuil Formation, overlying the Klipfontein Heuwel Formation, consists of stromatolitic dolomites as well as fenestral limestones with silicification being present but not as prevalent as in the underlying formation (Altermann and Siegfried, 1997). Overlying the Papkuil Formation is the Klippan Formation, a predominantly stromatolitic and microbial laminated dolomite with some void-filling quartz (Altermann and Siegfried, 1997). The top of this formation is similar to that of the Fairfield Formation, with dolomite and chert breccias in a shale matrix (Beukes, 1987). The second youngest formation of the Campbellrand Subgroup is represented by dolomites, limestone and cherts of the Kogelbeen Formation which is overlain by the uppermost Gamohaan Formation (Altermann and Siegfried, 1997). The Gamohaan Formation, according to Altermann and Siegfried (1997), comprises stromatolitic mats and laminated carbonates and is capped by the Tsineng Member. The Tsineng Member constitutes a transitional zone between the dolomites of the Campbellrand Subgroup and the banded iron-formation of the Asbestos Hills Subgroup, and is composed of black shales and iron-rich cherts (Altermann and Siegfried, 1997).

The Asbestos Hills Subgroup comprises the older Kuruman Iron-Formation and the younger Griquatown Iron-Formation. However, a "solution collapse unconformity" (Gutzmer and Beukes, 1996a: 1439) exists, in some places, between the Campbellrand Subgroup and the overlying Kuruman Iron-Formation, on which the iron-formation has slumped into karstic sinkhole structures to develop folded to brecciated, so-called Manganore Iron Formation (Beukes, 1983). Dissolution of the manganese-rich Campbellrand dolomite causes residual build-up of insoluble material (mainly chert, manganese and lesser iron) to form the Wolhaarkop breccia (Beukes, 1983; Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). The resultant stratigraphy shows a gradational contact between the lower Wolhaarkop breccia and the overlying Manganore Iron Formation (Beukes, 1983). This should then reflect an increasing Mn-Fe ratio with increasing depth in this zone.

The Ghaap Group is capped by the siliciclastics and iron formation of the Koegas Subgroup (Tsikos and Moore, 2001). According to Beukes (1986), a period of uplift and erosion led to the development of a regional unconformity between the Ghaap Group and the lower-most formation of the Postmasburg Group that is the glacial Makganyene diamictite. The spatial scale of the

unconformity, however, has been disputed by Polteau *et al.* (2006) who observe that some areas show a conformable transition from the Koegas Subgroup to the overlying Makganyene Formation. The Makganyene Formation is, in turn, overlain by subaqueously deposited lavas of the Ongeluk Formation (Beukes, 1986). Conformably overlying the Ongeluk Formation is the economically significant Hotazel Iron-Formation. This formation comprises three sedimentary manganese units interbedded with iron-formation and makes up what is known as the Kalahari Manganese Field (Tsikos and Moore, 1997). These three manganese beds are shown in Figure 1.3.A.

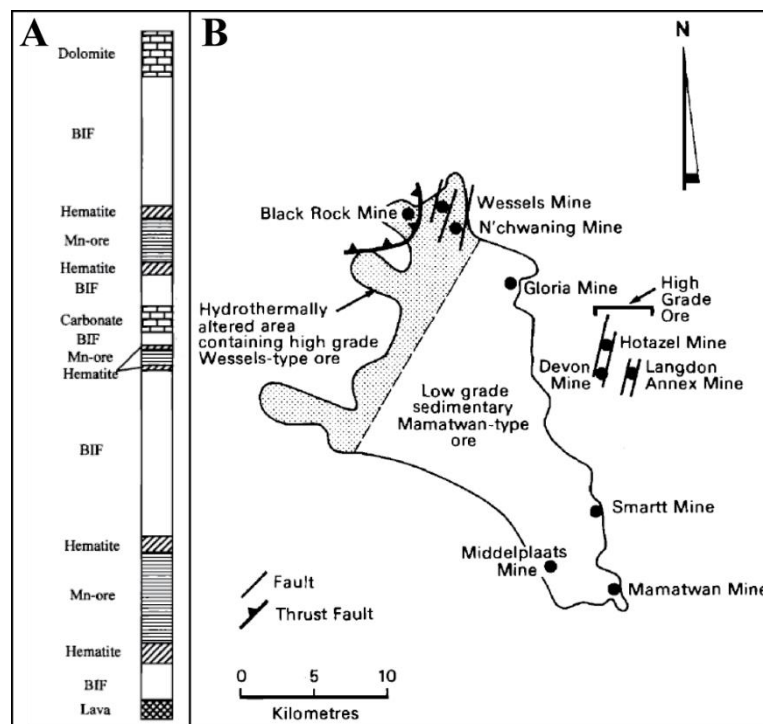


Figure 1.3: The Kalahari Manganese Field and manganese-hosting Hotazel Formation. A. Lithostratigraphic log of the Hotazel Formation and the base of the overlying Mooidraai Formation. B. Simplified map of the KMF showing the distribution of manganese ore grade and the location of mines (Both images modified after Tsikos and Moore, 1997).

Figure 1.4 shows a north-south cross section of the regional geology and the position of the PMF and KMF. This figure shows the truncation of the stratigraphy at the time of development of the regional unconformity (Beukes *et al.*, 2003). It was at this stage that lateritisation occurred.

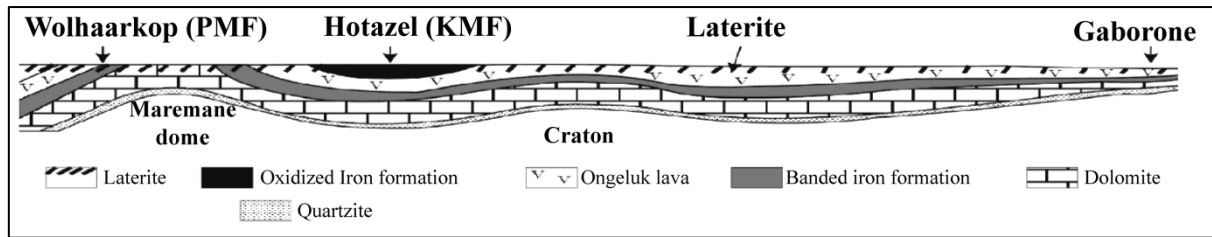


Figure 1.4: North-south geological cross section of the Transvaal Supergroup showing a regional unconformity cross-cutting the stratigraphy. The general positions of the PMF and KMF are also shown (modified after Beukes *et al.*, 2003).

Two broad classes of ore occur in the KMF:

1. Low-grade (max. ~ 40 % Mn) ore which is known locally as Mamatwan-type manganese ore after the Mamatwan Manganese Mine and consists predominantly of braunite (Nel *et al.*, 1986). This ore is affected only by low-grade metamorphism, if at all (Nel *et al.*, 1986). Thus the ore contains carbonates such as kutnahorite and Mn-calcite in the form ovoids and other concretionary structures (Nel *et al.*, 1986).
2. High-grade (max. ~60 % Mn), Wessels-type ore contributes a small portion of the total reserves in the KMF (Nel *et al.*, 1986). This ore is carbonate-poor and ore minerals include Ca-rich braunite (braunite-II), hausmannite and bixbyite (Nel *et al.*, 1986). Upgrading of this ore type has been attributed to metasomatic effects related to fault-controlled hydrothermal fluid flow by Gutzmer and Beukes (1995). Later work by Tsikos *et al.* (2003), however, indicates that a regional angular unconformity which crosscuts the Transvaal Supergroup may also be responsible for carrying fluids that aided in the upgrading of the Hotazel Formation manganese deposits.

The distribution of these ores is illustrated in Figure 1.3.B. Atop the Hotazel Formation and capping the Transvaal Supergroup is the carbonate-dominated Mooidraai Formation. The regional angular unconformity occurs between the Transvaal Supergroup and the overlying, basal Mapedi Formation of the Olifantshoek Supergroup and this unconformity has been variously linked to upgrading of iron (e.g. the giant Sishen deposit) and manganese (e.g. the Glossam deposit) ores in the region (Beukes, 1986; Gutzmer and Beukes, 1996a; Astrup and Tsikos, 1998; Tsikos *et al.*, 2003; Moore *et al.*, 2011). The Mapedi Formation in the northern part of the Transvaal Supergroup has been correlated to the Gamagara Formation in the southern part by Beukes and Smit (1987). A regional thrust fault occurs along the western edge of the Maremane dome and KMF and is thought to have been the

conduit for hydrothermal upgrading of manganese ores (Beukes, 1986). A vast area of the geology described above is covered by Late Phanerozoic sand and calcrete of the Kalahari Group.

1.2. **The Postmasburg Manganese Field**

Manganese ore deposits were first discovered near Postmasburg in 1922 by Cpt. L.T. Shone and these deposits became South Africa's largest source of manganese (Gutzmer, 1996). Mining in the PMF ceased completely in 1989 as a result of the success of mining in the even larger KMF (Gutzmer, 1996). Some of the historically major manganese mines in the area are the Lohatlha, Glosam and Bishop mines. However, some mining is taking place in the area on a small-scale today. The PMF occurs in two belts which stretch for approximately 65 km between Postmasburg and Sishen (De Villiers, 1960; Gutzmer and Beukes, 1996a; Astrup and Tsikos, 1998). A regional anticlinal structure occurs between Postmasburg and Sishen known as the Maremane dome which, for the most part, consists of the Campbellrand Subgroup carbonates (Astrup and Tsikos, 1998). The two belts refer to the Eastern and Western Belts as described in detail by De Villiers (1960). Although De Villiers (1960) provides detailed descriptions on the ores of the PMF, the more current descriptions provided by Plehwe-Leisen and Klemm (1995) and Gutzmer and Beukes (1996a, 1997) are focused on in the following section.

1.2.1. *Ferruginous ores of the Western Belt*

The ferruginous-type ores of the Western Belt occur within palaeosinkholes in the chert-free Reivilo Formation (otherwise known as the Ulco Member, according to SACS [1980]) of the Campbellrand Subgroup (Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). The hanging wall of these ores consists of Doornfontein conglomerates of the Gamagara Formation – the contact of which is gradual and conformable (Gutzmer and Beukes, 1996a). The ores increase in thickness with increasing depth of karstic depressions (Gutzmer and Beukes, 1996a). According to Plehwe-Leisen and Klemm (1995), the manganese-bearing Reivilo Formation underwent karstification before the deposition of the Gamagara Formation. They maintain that weathering and dissolution of the Reivilo Formation led to the deposition of residual, Mn-rich oozes. The concentrations of

manganese in such oozes are highest at the base of the orebody and decrease upwards (Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). Where the Doornfontein conglomerates are not developed above the manganese ore, iron-rich and aluminous shales have been deposited (Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). Gutzmer and Beukes (1996a) suggest that reactivation of karstic processes after lithification of the manganese ores caused slumping and brecciation of the ore in some areas.

Gutzmer and Beukes (1996a) distinguish three types of ferruginous manganese ore:

1. Ore that consists of fine-grained partridgeite and braunite in well-preserved sedimentary laminae and bedding. This ore also contains high aluminium concentrations represented by abundant lithiophorite. It occurs in beds up to 50 cm thick.
2. Irregular bodies of coarse-grained, bixbyite-rich ores which range from massive to highly vuggy.
3. Recent supergene ore consisting of pyrolusite, romanechite and cryptomelane.

Plehwe-Leisen and Klemm (1995) do not make the above distinction for the ferruginous Western Belt ores, preferring the provision of an all-inclusive description.

1.2.2. Siliceous ores of the Eastern Belt

The siliceous ores of the Eastern Belt are intimately associated with the Wolhaarkop chert breccia and the Fairfield Formation of the Campbellrand Subgroup (Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). The ore is capped by the Manganore Iron Formation which has slumped into the karstic sinkholes (Gutzmer and Beukes, 1996a). According to Gutzmer and Beukes (1996a), the matrix of the breccia is composed of quartz, hematite and braunite, becoming more siliceous and ferruginous toward the top and more manganiferous toward the base. Gutzmer and Beukes (1996a) describe transition zones between chert breccia and manganese ore bodies as gradual and characterized by a rapid increase in the manganiferous matrix to chert fragment ratio. Cross-cutting veins of coarse barite, globular hematite as well as pyrolusite have been described, as well as replacement of chert fragments by barite (Gutzmer and Beukes, 1996a). The mineable manganese ores predominantly consist of braunite and tend to be found at the contact between the chert breccia and the underlying dolomite (Gutzmer and Beukes, 1996a). These ores are massive and may contain cryptomelane and goethite vug-fills lined by euhedral braunite crystals (Gutzmer and Beukes,

1996a). Gutzmer and Beukes (1996a) mention the possible presence of thin hematite-rich illitic shale beds whereas Plehwe-Leisen and Klemm (1995) give mention to lens-shaped, laminated manganiferous clay intercalations.

1.2.3. Mixed ores

Plehwe-Leisen and Klemm (1995) describe a mixed ore type which occurs at the northern and southern ends of the Gamagara ridge. Gutzmer and Beukes (1996a), however, do not provide a separate characterization for this type as they consider it to be very similar to the Eastern Belt ore type. Plehwe-Leisen and Klemm (1995) also show the Mixed Type ore bodies to be comparable to those of the Eastern Belt with braunite being the major ore developed in both Wolhaarkop breccia and intercalated shales. The Eastern Belt paragenesis is ascribed to the Mixed Type ores by Plehwe-Leisen and Klemm (1995).

1.3. Previous work on the genesis of PMF ores

The genesis of the PMF ores has been a topic of contention over the years. Hall (1926) excluded a direct igneous or metamorphic origin for the deposits. Instead the author offered a replacement process whereby clay material is replaced by manganese oxides as a result of circulation of manganiferous fluids. Nel (1929) also discounted an igneous source, preferring metasomatic replacement of the original rock by manganese phases due to manganiferous fluids. Nel (1929) attributed the source of the manganese to the underlying dolomites.

In 1931, two authors, namely E. Kaiser and H. Schneiderhöhn, independently suggested that the ores are of sedimentary origin and that the manganese was deposited as the basal portion of the Gamagara Formation. This was soon discounted by du Toit (1933) who, instead, favoured supergene processes being responsible for ore formation with meteoric fluids responsible for dissolving the dolomite and carrying the manganese to replace surrounding country rock.

De Villiers (1944) suggested a hydrothermal origin for the PMF ores. The basis for De Villiers' (1944) arguments is the presence of bixbyite, ephesite, jacobsonite, acmite (aegirine), albite and apatite; all of which, according to the author, form under relatively high temperature. De Villiers (1944)

further suggested that the source of the hydrothermal fluid is magmatic, given the presence of lithium, sodium, boron and chlorine in the ores. This fluid was said to leach manganese from the manganese bearing dolomites of the Campbellrand Subgroup.

De Villiers (1960) dismissed a magmatic hydrothermal origin for the ores on the premise that there are no plausible sources for magmatic fluids in the area. De Villiers (1960) suggested that the aforementioned elements must have therefore been scavenged from the surrounding country rock. Furthermore, these minerals are not necessarily diagnostic of high-temperature conditions. De Villiers (1960), being a proponent of the supergene origin of the PMF ores, suggested that the Wolhaarkop breccia represented residual material resulting from leaching of tectonically brecciated dolomite. Leaching occurred as a result of groundwater flow through breccia fractures. De Villiers (1960) further suggested that during the leaching of the carbonate, manganese was also brought into solution and then deposited in the breccia and elsewhere. At a later stage, manganese was leached out of the dolomite which was exposed to supergene conditions as a result of slumping of the overlying breccia (De Villiers, 1960). More recent work on the PMF ores has been done by Plehwe-Leisen and Klemm (1995) and Gutzmer and Beukes (1996a). These authors provide separate models for the genesis of the ores of the Eastern and Western Belts which are outlined below.

1.3.1. Genesis of the Western Belt or ferruginous ores

The ores of both the Eastern and Western Belt required a karstic environment and the inherent sinkholes in order to form and be preserved (Plehwe-Leisen and Klemm, 1995). The ores of the Western Belt were deposited within karstic sinkholes developed in the Reivilo Formation of the Campbellrand Subgroup (Gutzmer and Beukes, 1996a). The Reivilo Formation is chert-free and manganiferous and would thus be suitable to form silica-poor ores of the Western Belt. This formation contains 2-3 wt. % MnO on average (Plehwe-Leisen and Klemm, 1995). Gutzmer and Beukes (1996a) suggest that the ores were deposited under surficial karstic conditions as evidenced by the presence of interbedded aluminous shales and hematite conglomerates, sedimentary bedding in the ores and the conformable contact between the ores and the overlying Gamagara Formation. Gutzmer and Beukes (1996a) indicated that the ferruginous ores of the PMF may have formed under lateritic conditions similar to Miocene ferromanganiferous ores in Hesse, Germany. The high aluminium contents and low Si/Al ratios of the ferruginous ores, as well as the presence of Al-silicate minerals, are indicative of a lateritic provenance (Gutzmer and Beukes, 1996a). Low Na,

Mg, Cu, Ni and Co in the ores is said to be indicative of a fresh-water karstification process (Gutzmer and Beukes, 1996a). Ore minerals, as presently seen in the ferruginous type, according to Gutzmer and Beukes (1996a), are as a result of diagenesis and low-grade metamorphism.

Plehwe-Leisen and Klemm (1995), however, consider two types of mineralization for the ferruginous ores that formed at differing time periods. The first type is the “basal type” which is located in the lower portions of sinkhole structures, adjacent to the dolomite. This ore type bears the highest concentration of manganese and is said to be residual along with karstic clays. The second type is located higher up and is more iron-rich. It is finely layered and is “intercalated with mineralized shales” (Plehwe-Leisen and Klemm, 1995: 266). Plehwe-Leisen and Klemm (1995) interpret this type as having been precipitated from sea water after the transgression of the Transvaal sea. These interpretations are solely based upon a mineralogical study of the ores. Plehwe-Leisen and Klemm (1995) place little emphasis on geochemical data save for a few comments on Eh and pH of circulating fluids based upon work of other authors.

1.3.2. Genesis of the Eastern Belt or siliceous ores

The siliceous ores of the Eastern Belt are related to the chert- and manganese-bearing Fairfield Formation which has an average of 1-3 wt. % MnO (Plehwe-Leisen and Klemm, 1995). Gutzmer and Beukes (1996a) suggest that siliceous ores were formed as a result of dissolution of carbonate and residual enrichment of manganese in cave systems below lithified banded iron-formation of the Asbestos Hills Subgroup. The banded iron-formation slumped into the developing cave system (forming the so-called Manganoir Iron Formation) but dissolution continued to progress downward into the underlying dolomite thus forming a locally inverted stratigraphy (Gutzmer and Beukes, 1996a). Gutzmer and Beukes (1996a) further indicate that the relative amount of chert clasts to residual manganese would be dependent upon the local composition of the dissolving dolomite. Later diagenesis and low grade metamorphism led to recrystallization of residual manganese to a braunite-partridgeite assemblage. Plehwe-Leisen and Klemm (1995) believe that the dissolution of the Fairfield Formation started before the deposition of the Asbestos Hills Formation and that deposition of the BIF occurred atop open karstic sinkholes.

1.4. **Metamorphism and Hydrothermal Activity**

De Villiers (1944) suggested a hydrothermal origin for the PMF ores, stating that the presence of a number of minerals, particularly bixbyite, was indicative of high-grade metamorphism. The author also suggested that the presence of certain elements (e.g. Br and Cl) is indicative of a magmatic source for hydrothermal fluids. De Villiers (1983) used the iron content of bixbyite as a geothermometer where higher iron content reflects bixbyite formation at higher temperatures. The results of the study, however, were inconclusive, with iron content of bixbyite in the PMF ranging from 0.5 wt. % to 21.9 wt. %. Thus the calculated temperatures from various localities in the PMF ranged from under 120°C to 470°C (De Villiers, 1983). Nell *et al.* (1994) reinforce the idea of using bixbyite as a geothermometer but also point to a fair amount of uncertainty when applying their method (based on the distribution of iron in the bixbyite structure) to natural bixbyite. Nevertheless, Nell *et al.* (1994) found that two bixbyite grains from the PMF showed temperatures of formation of 315°C and 370°C. Plehwe-Leisen (1985) also estimated that the metamorphic temperatures for the PMF range between 350°C and 400°C. These temperature ranges seem to point to lower greenschist facies metamorphism in the area (Gutzmer and Beukes, 1996a).

Hydrothermal fluid flow and resultant metasomatic effects on the ores of the PMF have been shown by Moore *et al.* (2011). Moore *et al.* (2011) describe rare silicates such as sugilite, armbrusterite and norrishite as well as more common minerals such as albite and K-feldspar in Mn-rich occurrences above the Wolhaarkop breccia from Bruce Mine, which all suggest alkali metasomatic effects in the PMF area.

As to the timing of metamorphism in the Postmasburg manganese field, Gutzmer and Beukes (1996a) suggest an age of 1.8 to 1.9 Ga, during the Kheis orogeny. The regional Black Ridge thrust fault on the western edge of the PMF is said to have formed during this time (Gutzmer and Beukes, 1996a). However, a tentative sugilite ^{40}Ar - ^{39}Ar age of 620.2 ± 3.3 Ma determined by Moore *et al.* (2011) suggests that a much later hydrothermal alteration event may have occurred in the area, possibly on a regional scale.

1.5. **Research Aims and Objectives**

Research pertaining to the Postmasburg Manganese Field has mainly, up until now, focussed on samples collected throughout the PMF from existing surface outcrop and mine workings. Apart from the work by Moore *et al.* (2011), little to no analyses have been performed on samples retrieved from manganese ores from vertical diamond drill core sections. It is from these diamond drill cores that valuable information can be gained as these have been unaffected by current weathering processes and also provide a definite picture of the underlying stratigraphy. Furthermore, mineralogical studies have predominantly focused on the ore minerals and little emphasis has been placed upon the significance of gangue phases.

This study aims to contribute further to the existing knowledge regarding the character and genesis of PMF ores. It also stands to make a valuable contribution by simply using diamond drill core samples as opposed to near-surface grab samples. Detailed petrography, particularly of gangue phases but also of ore minerals, coupled with bulk and mineral-specific geochemical data, will aid in elucidating processes and even perhaps timing of ore formation. Thus the objectives of the study include:

1. Mineralogical and geochemical characterization of PMF ore bodies by petrographic, mineral chemical and various geochemical techniques.
2. Assessment of the potential for regional scale alkali-rich fluid flow by comparison to previous work.
3. Evaluation of existing genetic models for PMF mineralization.

The thesis consists of a description of the samples and core logs in Chapter 2, petrographic descriptions and mineral-chemical data in Chapter 3, bulk geochemical and stable isotope data in Chapter 4 and a discussion of results and conclusion in Chapter 5. This is followed by a list of references and appendices.

Chapter 2

Sample selection, drill core logs and methods

2.1. Introduction

Work on the PMF ores has, to a large extent, focused on outcrop-based and mine-based sampling (e.g. De Villiers, 1960; Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). Very little work has been done on diamond drill cores which provide much clearer and well-defined stratigraphic profiles. The study by Moore *et al.* (2011) was undertaken on a diamond drill core (drill core AKH49) but this seems to be the only study that makes use of such a valuable resource. The present study focuses on four vertically drilled diamond drill cores including the core studied by Moore *et al.* (2011), a log of which can be found in the latter publication and in Appendix II. The other three diamond drill cores were selected at the Kumba Iron Ore exploration camp. The criteria for selection were as follows:

- Two of the cores must show typical stratigraphy for PMF ores and at least one core must have intercepted the Campbellrand dolomites.
- The manganese ores must show vuggy textures (indicating the influence of fluid influx) with vug-filling silicates.
- Intersections affected by apparent faulting/brittle fracturing or containing igneous intrusive units must be avoided.

The three cores that were selected are SLT-015, SLT-017 and SLT-018. Hand-specimen observations and detailed logs of the three cores are presented in the following sections.

2.2. Diamond drill core SLT-015

This drill core is the main focus of the thesis as the ore is typically vuggy and bears an abundance of void-filling minerals. It also shows the typical stratigraphy of the Eastern Belt ores with Wolhaarkop breccia at the base. This is shown in Figure 2.1. This figure provides a broad stratigraphy and contextualizes the Wolhaarkop breccia and related ferromanganese ore in drill core SLT-015.

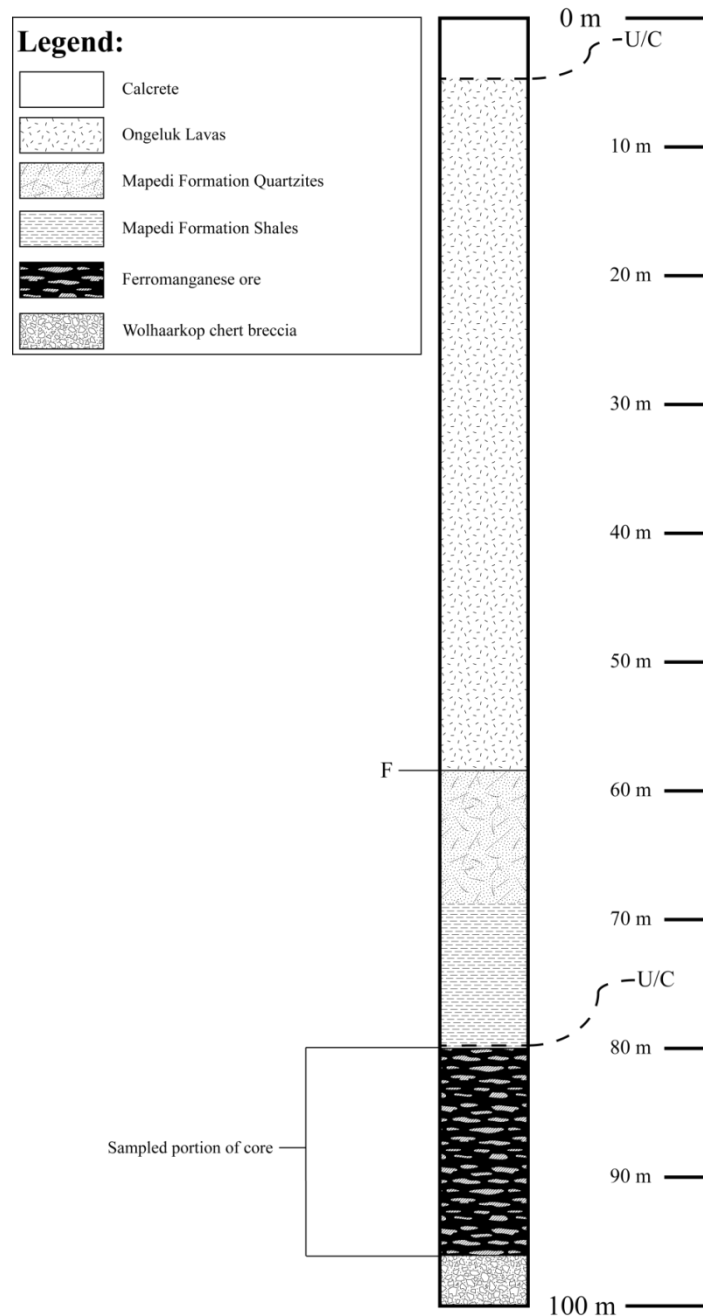


Figure 2.1: Broad stratigraphic log of drill core SLT-015.

The base of the core consists of clast-supported Wolhaarkop breccia. This grades into the ferromanganese ore. The ore is unconformably overlain by Mapedi Formation shales and quartzites. This is the angular unconformity that is believed to be responsible for the regional upgrading of various iron and manganese ore bodies as discussed in Chapter 1. Thrusted over the quartzite unit of the Mapedi Formation is the andesitic lava flow of the Ongeluk Formation. This thrust forms part of

the Black Ridge thrust which occurs on a regional scale. Finally, at the top of the drill core is 4 meters of Kalahari Group calcrete. The depth at which the top of the orebody is intersected is around 80 m from the surface. At such a depth the influence of surficial weathering is expected to be negligible. Below is a detailed description of the sampled section of drill core SLT-015.

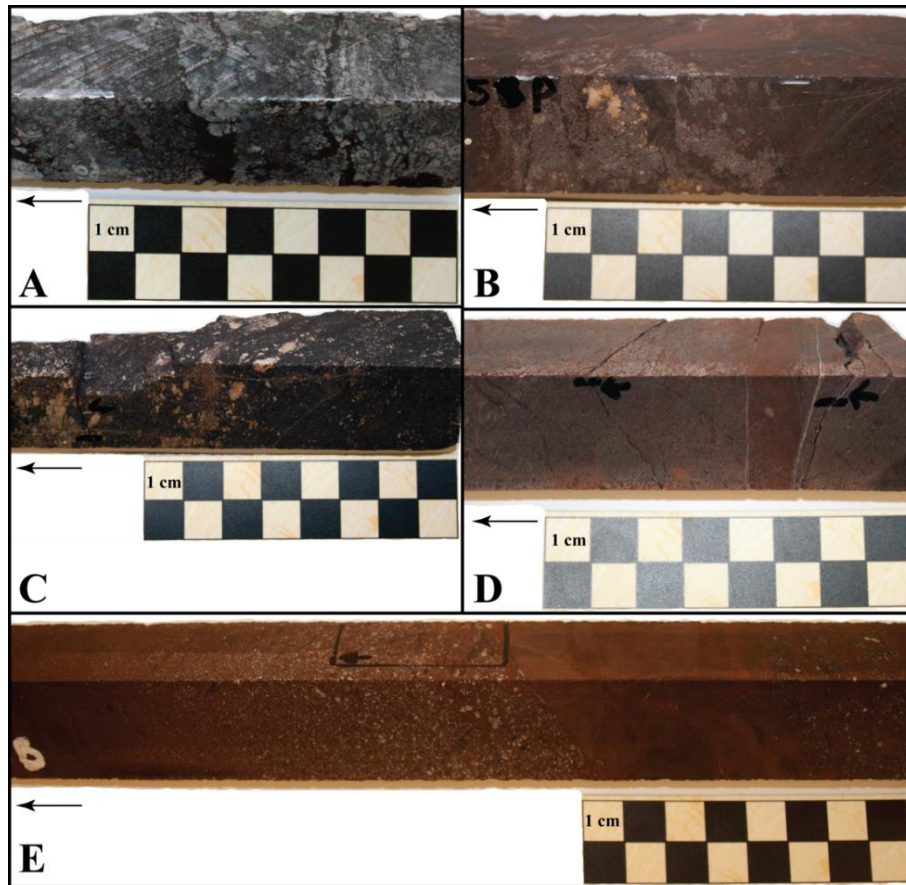


Figure 2.2: Hand specimens of representative samples of some of the units in SLT-015. Arrows indicate decreasing stratigraphic depth. **A.** Clast-supported, chert breccia at the base of the drill core (sample 15-25). **B.** Vuggy ferromanganiferous matrix (sample 15-15P). **C.** Coarse-grained, vuggy manganese ore (sample 15-15I). **D.** Brick-red hematite lutite with pervasive, grey, extremely fine-grained mineral (sample 15-09). **E.** White fragments (up to 2 mm in size) in fine-grained ore matrix (sample 15-15E).

The sampled section in diamond drill core SLT-015, as shown in Figure 2.3 reaches a depth of approximately 98 m below surface. It is at this point that the base of the Wolhaarkop breccia is developed. The breccia shows a general fining-upward trend of chert clasts. At the base the breccia is clast supported with clasts consisting of chert and polyhedral quartz grains up to 0.5 mm in size

(Figure 2.2.A). From 97 m to ~95 m the core consists of vuggy ferromanganiferous matrix which grades back into clast-supported chert breccia with minor matrix until ~ 92.5 m. Here the breccia disappears almost entirely giving way to vuggy ferromanganiferous ore as in Figure 2.2.B. This grades into coarse-grained, highly vuggy manganese ore with abundant vug-filling, fine-grained, white to yellow minerals (Figure 2.2.C). At ~ 91 m, the vuggy texture of the ore gives way to massive ore with coarse-grained pods of manganiferous material as well as interstitial very dull brownish red matrix. This ore continues until a depth of ~ 88 m and also bears some brick red, lutaceous lenses as well as minor very fine-grained pebble layers. The depth of 88 m is marked by the appearance of an abundance of coarse (up to 2 mm), white fragments in a fine-grained brick-red matrix. This is interlayered with thin, massive, apparently manganese-rich layers. The top bed of this clast bearing rock is approximately 10 cm thick and shows a fining-upward of the clasts until only matrix is present at ~ 87.40 m (Figure 2.2.E). This grades into crudely laminated ore with darker, more ferromanganiferous layers alternating with dark brick-red layers (assumed to be more siliceous due to the lighter appearance relative to the ferromanganiferous layers). This laminated ore grades into dark brick-red, hematite lutite which seems to be siliceous as it contains extremely fine-grained greyish material (Figure 2.2.D). Finally, at the top of the sampled section the hematite lutite grades into crudely laminated ferromanganese ore and brick-red lutite. At hand specimen scale, many of the features described above appear to be of clastic nature. However, petrographic observation of these features indicates the influence of post-depositional processes as discussed in Chapter 3.

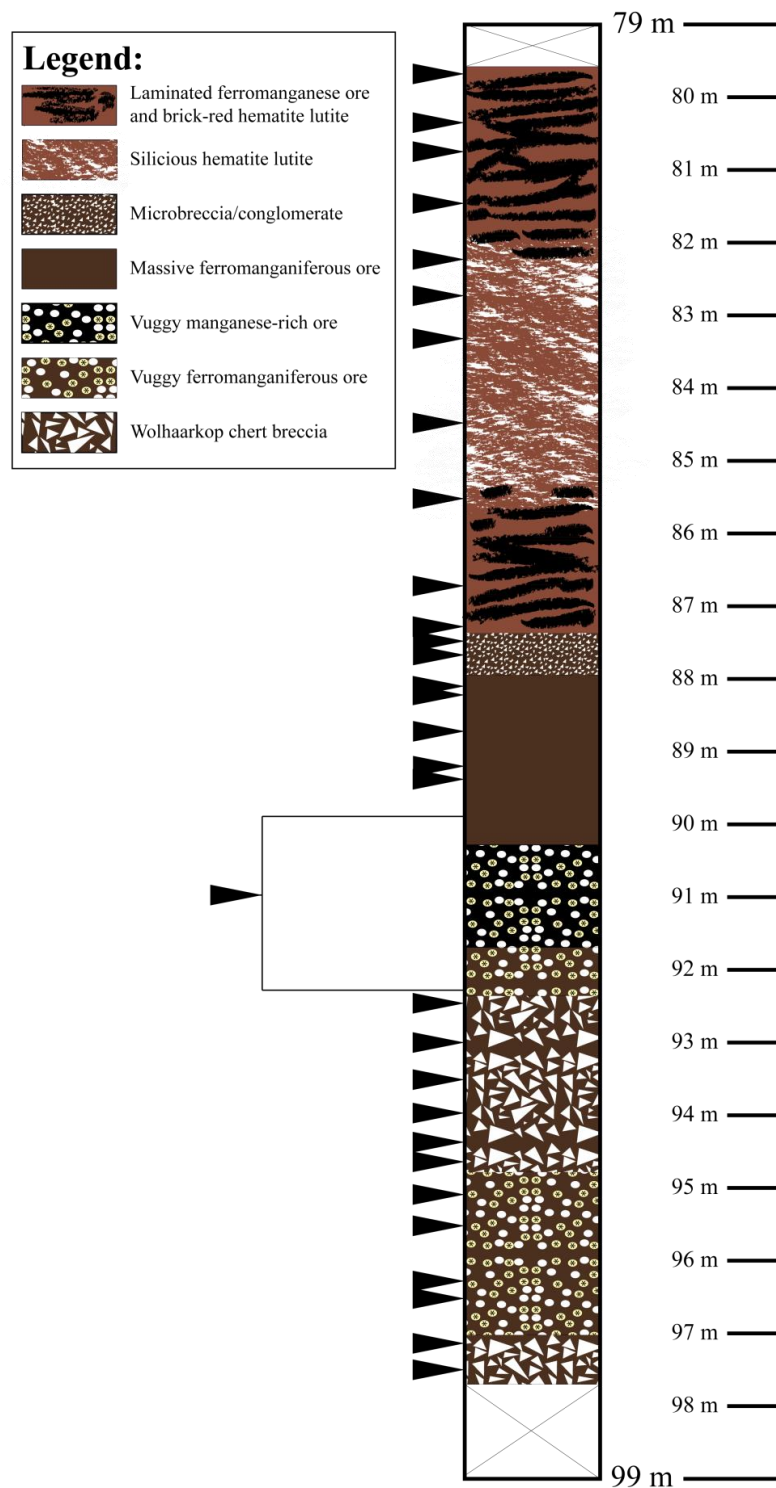


Figure 2.3: Detailed stratigraphic log of the sampled section of diamond drill core SLT-015. Arrows alongside the log indicate sample positions.

2.3. Diamond drill core SLT-017

Figure 2.3 shows the log of diamond drill core SLT-017. The bottom of the drill core is at a depth of 130 m below surface. The basal part of the core, from 130 m to ~ 119 m, consists of chert breccia with the number of chert clasts decreasing upwards. The matrix consists of black to dull brownish-red ferromanganiferous wad. At ~ 119 m, some core loss has occurred most likely due to the presence of a fault.

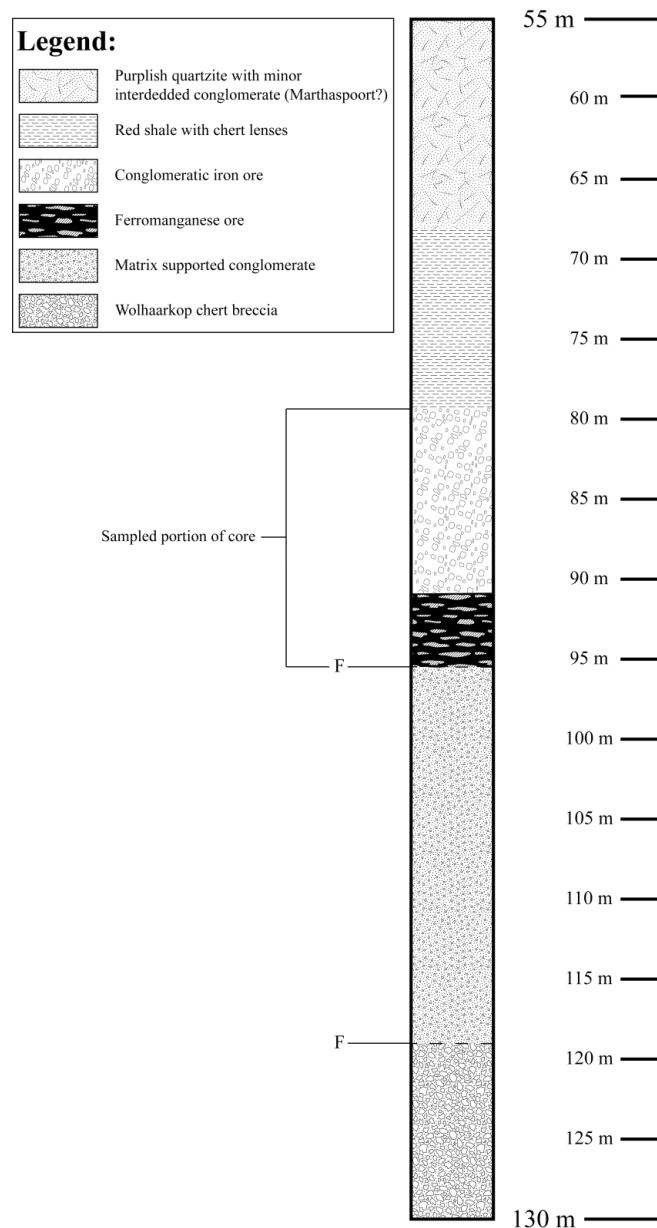


Figure 2.3: Simplified stratigraphic log of diamond drill core SLT-017.

The overlying ~25 m consists of matrix-supported conglomerate. The matrix to clast ratio is high and the matrix consists of purplish quartzite. The clasts comprise quartz as well as banded iron-formation (both ferruginised and unferruginised). The top contact of this conglomerate is represented by a fault which is evident due to core loss and the presence of slickensides on some fragments at a depth of ~ 95 m. Overlying this is ferromanganese ore. This consists of generally extremely fine-grained, laterally discontinuous and ‘wispy’ layers of alternating manganiferous and ferruginous material. The top of the orebody, at ~ 90.85 m, is marked by an abrupt contact with overlying ferruginised conglomerate. This conglomerate tends to be clast-supported, where clast size is greater than about one centimetre, and matrix supported where clasts are smaller than one centimetre. However, the conglomerate is generally poorly sorted thus this distinction is only a rough guideline. Clasts consist of ferruginised banded iron-formation and range in roundness from angular to well-rounded. A gradual transition exists between the conglomerate and the overlying red shales with the ‘contact’ placed at around 79 m. The shale grades into purplish quartzite over a gradational contact between ~ 68 m and ~ 65 m. The quartzite contains minor interbedded conglomerates with ferruginised banded iron-formation clasts. The remaining 55 m of core consist of shale and calcrete. The base of the ferromanganese ore upwards represents the ‘ideal’ stratigraphy for ferruginous ores of the Western Belt. Samples were taken from the ferromanganese ore and the conglomeratic iron ore at regular intervals.

2.4. Diamond drill core SLT-018

This drill core intercepts Campbellrand dolomites at the bottom of the core. Seven samples were retrieved from the dolomites with caution taken to avoid siliceous domains. These domains were avoided so as not to contaminate the carbonate during bulk-rock stable isotope analysis. The dolomites are brecciated toward the top and grade into a chert breccia with a reddish brown clay matrix. A melange of rock types exist above the breccia. The rock types range from slivers of conglomeratic iron ore to ferromanganese ore to interbedded shales and quartzites. Large amounts of core loss and abundant fragmentation and fracturing in the core above the breccia exists. The abundant core loss and irregular stratigraphy suggests abundant faulting, also making sampling above the dolomites a meaningless exercise.

Chapter 3

Petrography and Mineral Chemistry

3.1. Introduction and previous work

Most petrographic and mineral chemical work on the Postmasburg Manganese Field has involved detailed observation of ore minerals (De Villiers, 1960; Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a; Gutzmer and Beukes, 1997). Other than the work by Moore *et al.* (2011), little emphasis is placed upon gangue phases even though these phases may show key relationships to ore phases that provide insight into mineral paragenesis and ore genesis. The determination of the nature of hydrothermal or similar activity, for instance, may be aided by analysis of gangue phases. This section aims to provide in-depth observations of the ore and gangue phases found in PMF ores. Each drill core, as outlined in Chapter 2, is described separately and stratigraphically from bottom to top. For simplicity, ore minerals and opaque phases are described as the matrix or ore minerals and the transparent phases are referred to as the gangue phases. Before presenting the petrographic observations of the present study, it is useful first to highlight the petrographic observations conducted by previous authors working on the PMF ores. Arguably the most comprehensive petrographic descriptions of recent times are those reported by Gutzmer and Beukes (1996a; 1997). The meaning of abbreviations which appear in the following section can be found in the list of abbreviations in Appendix I. Also, individual microprobe analyses can be found in Appendix IV.

3.1.1. Eastern Belt Siliceous Ores

Recrystallization of chert clasts to polygonal quartz in the Wolhaarkop breccia is commonplace (Gutzmer and Beukes, 1996a). As the ore is confined to the matrix, observing mineralogical changes within it is important. Gutzmer and Beukes (1996a) describe the matrix in the basal part of the Wolhaarkop breccia as being almost solely composed of braunite with only minor amounts of partridgeite, hematite and quartz. However, toward the upper part of the breccia, the matrix consists of fine-grained hematite and quartz. Gutzmer and Beukes (1996a) show that euhedral braunite grains occur in vugs and fractures with some grains showing distinct zonation. They also describe

very fine-grained partridgeite as well as rare intergrown partridgeite and braunite lamellae. Minor, accessory phases in this ore-type include apatite and barian muscovite as well as aggregates of aegirine and albite ($\text{Ab}_{94}\text{An}_6$) (Gutzmer and Beukes, 1996a). Gutzmer and Beukes (1996a) also describe a number of minerals related to supergene alteration such as ramsdellite, romanechite, cryptomelane, pyrolusite and lithiophorite.

Plehwe-Leisen and Klemm (1995) noticed variations in the reflection colour in the braunite grains in siliceous ores. After performing microprobe analyses on the braunite grains, they distinguished 2 populations of braunite based on their iron content (less than or equal to 1 wt. % and 5 wt. %). They attributed the iron-poor variety to secondary recrystallization of braunite in an iron-poor environment.

Moore *et al.* (2011) describe vug-fill mineralogy in the Wolhaarkop breccia at the Bruce iron-ore mine, south of Sishen in the broad area where Plehwe-Leisen and Klemm (1995) describe the Mixed Type manganese ore. Moore *et al.* (2011) describe rare minerals such as norrishite, sérandite, armbrusterite, witherite, strontianite, kentrolite and, in particular, the Na-K-Fe-Mn silicate, sugilite. These occur with more common minerals such as K-feldspar and albite as well as, in places, aegirine (Moore *et al.*, 2011). The study by Moore *et al.* (2011) formed the basis for the present research due to the need to explore further and assess the distribution of alkali assemblages in the Transvaal Supergroup in the Northern Cape Province.

3.1.2. Western Belt Ferruginous Ores

Fine-grained bedded ores of the ferruginous type, as described by Gutzmer and Beukes (1996a), consist of alternating braunite-partridgeite and ephesite-diaspore laminae. Microconcretions composed of partridgeite and/or braunite are present in the braunite-partridgeite laminae (Gutzmer and Beukes, 1996a). Gutzmer and Beukes (1996a) also describe microconcretions of diaspore, ephesite and lithiophorite which have rims of hematite, braunite or partridgeite. These concretions are found in the shaly laminae of diaspore and ephesite (Gutzmer and Beukes, 1996a). Rare hematite concretions are also described. Gutzmer and Beukes (1996a) attribute aluminium in massive beds of aluminous manganese ores to supergene lithiophorite.

Coarse-grained ores, also described by Gutzmer and Beukes (1996a), consist of coarse-grained bixbyite intergrown with hematite and braunite. Diaspore, ephesite and amesite fill vugs and pore

spaces (Gutzmer and Beukes, 1996a). Iron content of the bixbyite ranges from 10 to 22 wt. % Fe_2O_3 (Gutzmer and Beukes, 1997). In some cases coarse-grained barite is present in association with diasporite (Gutzmer and Beukes, 1996a).

Supergene ores are dominated by romanechite which develops as cauliflower aggregates, botryoidal crusts and boxwork textures (Gutzmer and Beukes, 1996a). Wad layers are predominantly composed of X-ray amorphous manganese oxides (Gutzmer and Beukes, 1996a).

3.2. **Diamond Drill Core SLT-015**

This drill core is the most important of the four drill cores as hand specimens show large amounts of vug-filling minerals and the Wolhaarkop breccia is well developed.

3.2.1. *Summary of Analytical Methods*

Thin sections and polished sections were cut from selected drill core samples based upon macroscopic observations which focussed on determination of representative samples but also on areas of particular interest such as those areas possessing coarse-grained vug-fill mineral assemblages. This allowed petrographic observations to be made using both transmitted and reflected light. Where identification of minerals was difficult by microscope, X-Ray Diffraction (XRD) and electron probe microanalyser (EPMA) techniques were adopted. Element mapping and mineral chemical analyses as well as semi quantitative analyses were undertaken using a JEOL JXA-8230 Superprobe at the Department of Geology, Rhodes University. Bulk-rock XRD analyses were performed on bulk rock powders (unless otherwise stated) using a Bruker D8 Discover XRD housed in the Department of Chemistry, Rhodes University.

3.2.2. Clast-supported chert breccia

At the base of the drill core (Figure 3.1), where the breccia is clast supported, clasts are composed of chert. However, coarse (up to 2000 μm), polyhedral quartz grains are also present as well as chalcedonic textures that typify void-filling processes as discussed presently.

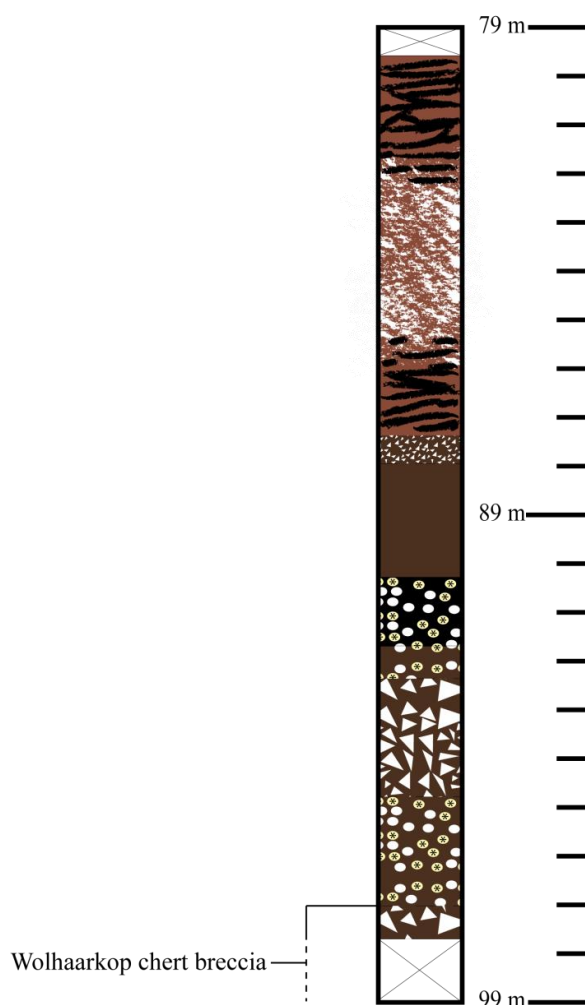


Figure 3.1: The position of the lowermost clast-supported chert breccia unit in SLT-015.

The matrix consists of extremely fine-grained hematite. Figure 3.2 shows the textures found in the lower part of the Wolhaarkop breccia. Figure 3.2.A shows a large vug at the base of the Wolhaarkop breccia with euhedral, coarse-grained quartz in its centre. The grain-size decreases toward the edge of the vug, finally terminating with chalcedony at the vug boundary. This is a common feature in this part of the stratigraphy and is indicative of open-space filling by quartz. Another common

feature is that of interlocking chert aggregates in a hematite matrix with little to no recrystallization of chert to euhedral grains as shown in Figure 3.2.B. The matrix predominantly consists of hematite with minor hydrous iron oxides. Figure 3.2.C shows this matrix – the hematite is finely laminated with laminations wrapping around chert clasts and quartz vugs.

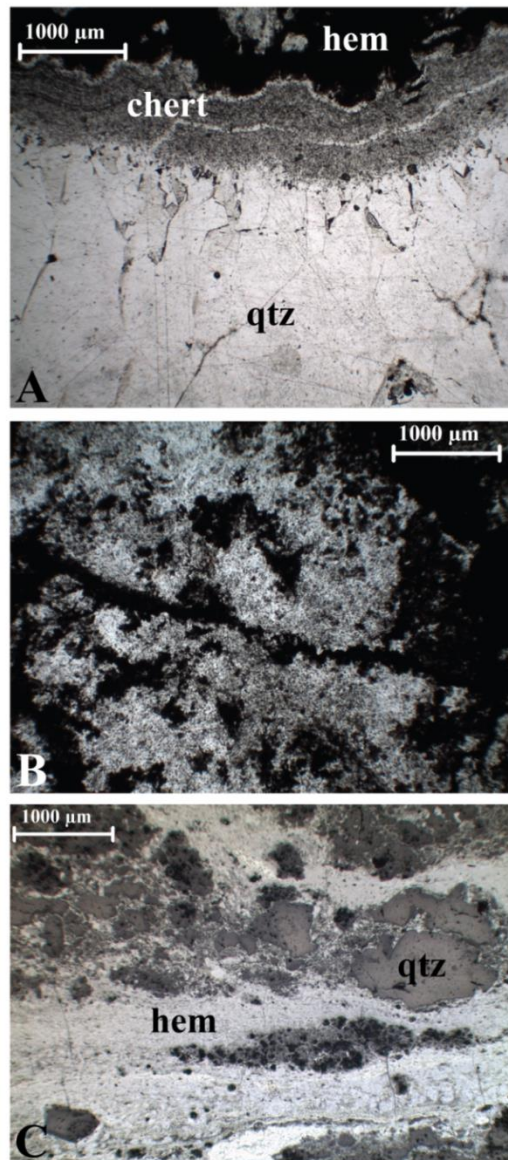


Figure 3.2: Photomicrographs of the lower portion of the Wolhaarkop breccia in drill core SLT-015. **A.** Clast with coarse-grained, euhedral quartz in the centre and chalcedony on the boundary as well as a hematite matrix (PPL, sample 15-26A). **B.** White, extremely fine-grained, interlocking chert in opaque (hematite) matrix (PPL, sample 15-26A). **C.** Fine-grained hematite matrix hosting quartz (reflected light, sample 15-25).

3.2.3. Matrix-supported, vuggy breccia

Approximately two meters of matrix-supported, vuggy breccia overlies the basal portion (Figure 3.3). The variety of mineral phases present in the rock increases greatly in this zone. Of particular interest is the presence of two rare minerals, namely noélbensonite and a similar mineral to the Ba-Mn vanadate tokyoite.

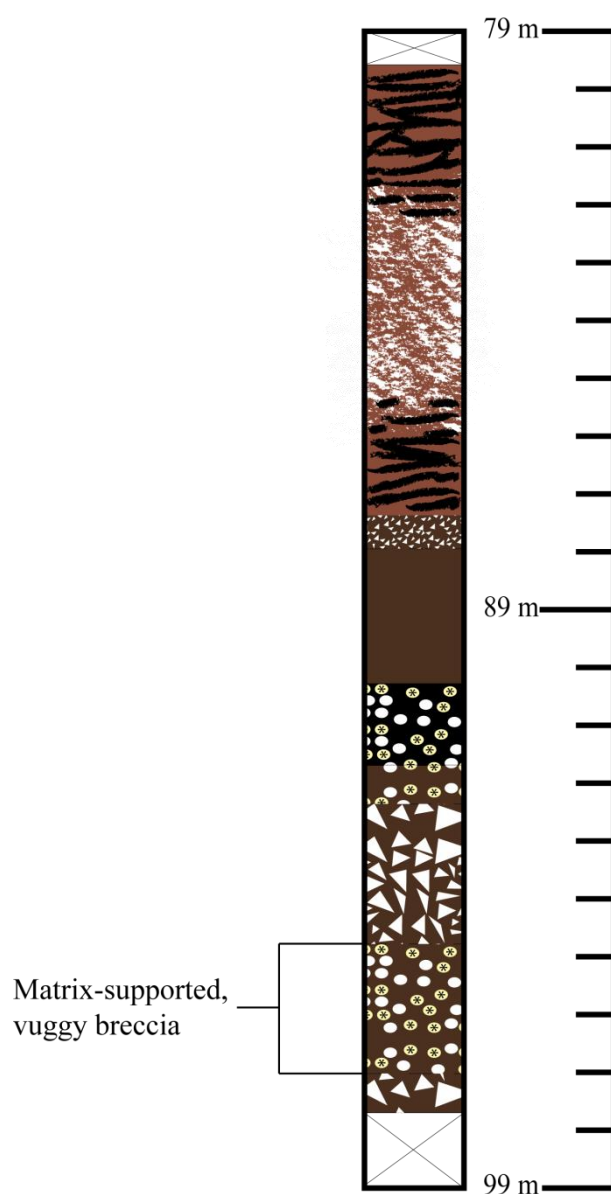


Figure 3.3: Log showing the stratigraphic position of the matrix-supported, vuggy breccia unit in SLT-015.

Noélbensonite, $\text{BaMn}_2^{3+}(\text{Si}_2\text{O}_7)(\text{OH})_2 \cdot \text{H}_2\text{O}$, was first described by Kawachi *et al.* (1996) from the Woods ornamental rhodonite mine in Australia. Kawachi *et al.* (1996) observed noélbensonite replacing Na-Mn amphibole, sérandite and namansilite in manganese-rich pods. It also occurs in fine veinlets and as fine disseminations and is said to have formed after the metamorphic maximum (Kawachi *et al.*, 1996). Only one other occurrence of noélbensonite has been confirmed and that is at the Cerchiara Mine in Italy (Kawachi *et al.*, 1996). The discovery of noélbensonite in the present study makes it the third occurrence of the mineral worldwide. Tokyoite, with the formula $\text{Ba}_2\text{Mn}^{3+}(\text{VO}_4)_2(\text{OH})$, was first described by Matsubara *et al.* (2004) from the (now abandoned) Shiromaru manganese mine in Japan. It was found in association with braunite, hematite, albite, aegirine, celsian, hyalophane and such rare minerals as cymrite and tamaite (Matsubara *et al.*, 2004). Matsubara *et al.* (2004) also describe veinlets of banalsite, barite, strontianite, sérandite, strontiapiemontite, marsturite and ganophyllite group minerals. The tokyoite occurs, at the type-locality, as very fine-grained aggregates and is said to have formed as a result of Ba- and V-bearing fluids in the presence of braunite (Matsubara *et al.*, 2004). It also occurs in veinlets in association with hyalophane and tamaite and cross-cutting braunite (Matsubara *et al.*, 2004).

The present study provides initial data on a similar mineral to tokyoite. This mineral, however, is an As-bearing Ba-Mn vanadate and will be called *arsenotokyoite* for the purpose of this study. The limited abundance and very fine-grained nature of the mineral and host rock has hindered the confirmation of the mineral by X-ray diffraction. Arsenotokyoite is composed of $\sim 7\%$ As_2O_5 as shown in Table 3.1. Arsenic substitutes for vanadium in the tokyoite structure. The simplified formula for arsenotokyoite would thus be $\text{BaMn}^{3+}[(\text{As},\text{V})\text{O}_4]_2(\text{OH})$. Deep reddish-brown arsenotokyoite is predominantly found in association with noélbensonite in SLT-015.

Table 3.1: Chemical composition of tokyoite from Shiromaru mine, Japan and arsenotokyoite from drill core SLT-015.

Oxide wt. %	Shiromaru ^a	15-23	15-23	15-23
V ₂ O ₅	31.77	27.51	26.78	27.12
As ₂ O ₅	n.d	7.10	7.40	7.06
SiO ₂	0.15	n.d	n.d	n.d
Al ₂ O ₃	0.07	n.d	n.d	n.d
Fe ₂ O ₃	2.33	n.d	n.d	n.d
Mn ₂ O ₃	11.27	12.95	13.49	13.85
CaO	0.07	n.d	n.d	n.d
BaO	51.91	49.91	50.20	50.01
SrO	0.22	n.d	n.d	n.d
Na ₂ O	0.13	n.d	n.d	n.d
H ₂ O*	1.59	1.80	1.76	1.77
Total	99.51	99.27	99.63	99.80
Cations calculated on the basis of 8.5 O:				
V	2.00	1.74	1.69	1.70
As		0.35	0.37	0.35
Si	0.01			
Al	0.01			
Fe	0.17			
Mn	0.82	0.94	0.98	1.00
Ca	0.01			
Ba	1.94	1.87	1.88	1.86
Sr	0.01			
Na	0.02			

^aMatsubara *et al.* (2004)

*Calculated according to the tokyoite mineral formula with As substituting for V; Key: n.d. = not determined.

Arsenotokyoite and noélbenzonite are found in association with sérandite as well as microcline, witherite and quartz. Sérandite has the formula $\text{NaMn}^{2+}_2\text{Si}_3\text{O}_8(\text{OH})$ thus forming the Mn end-member of the sérandite-pectolite series (Takeuchi *et al.*, 1976). This mineral is found in the KMF, at the Wessels high-grade manganese mine (Dixon, 1989) as well as further south at the Bruce iron-ore mine (Moore *et al.*, 2011). At the Bruce locality it is found in association with sugilite, albite, armbrusterite and norrishite as well as minor witherite (Moore *et al.*, 2011). Sérandite has also been reported from pegmatites of the Lovozero Alkaline Complex, Kola Peninsula, Russia (Pekov *et al.*, 2005). Witherite is the second most common Ba phase on Earth and tends to occur in association with barytoalcite and barite (Deer *et al.*, 1992). It typically occurs as low-temperature hydrothermal veins or as a replacement of barite (Deer *et al.*, 1992). In the lower portion of drill core SLT-015, sérandite, microcline, witherite and quartz fill vugs in a fine-grained matrix dominated by hematite with some braunite. The dominant vug-filling phase is witherite which mostly occurs as coarse (up

to 1000 μm), subhedral to euhedral grains (Figure 3.4). Figure 3.4.A shows microcline as it is typically found in this portion of the stratigraphy; that is as fine- to coarse-grained (up to ~ 500 μm) adularia-type grains lining the outer zone of vugs. In this case coarse (up to 300 μm) arsenotokyoite occurs in the core of the vug and noélbensonite seems to be pseudomorphously replacing microcline.

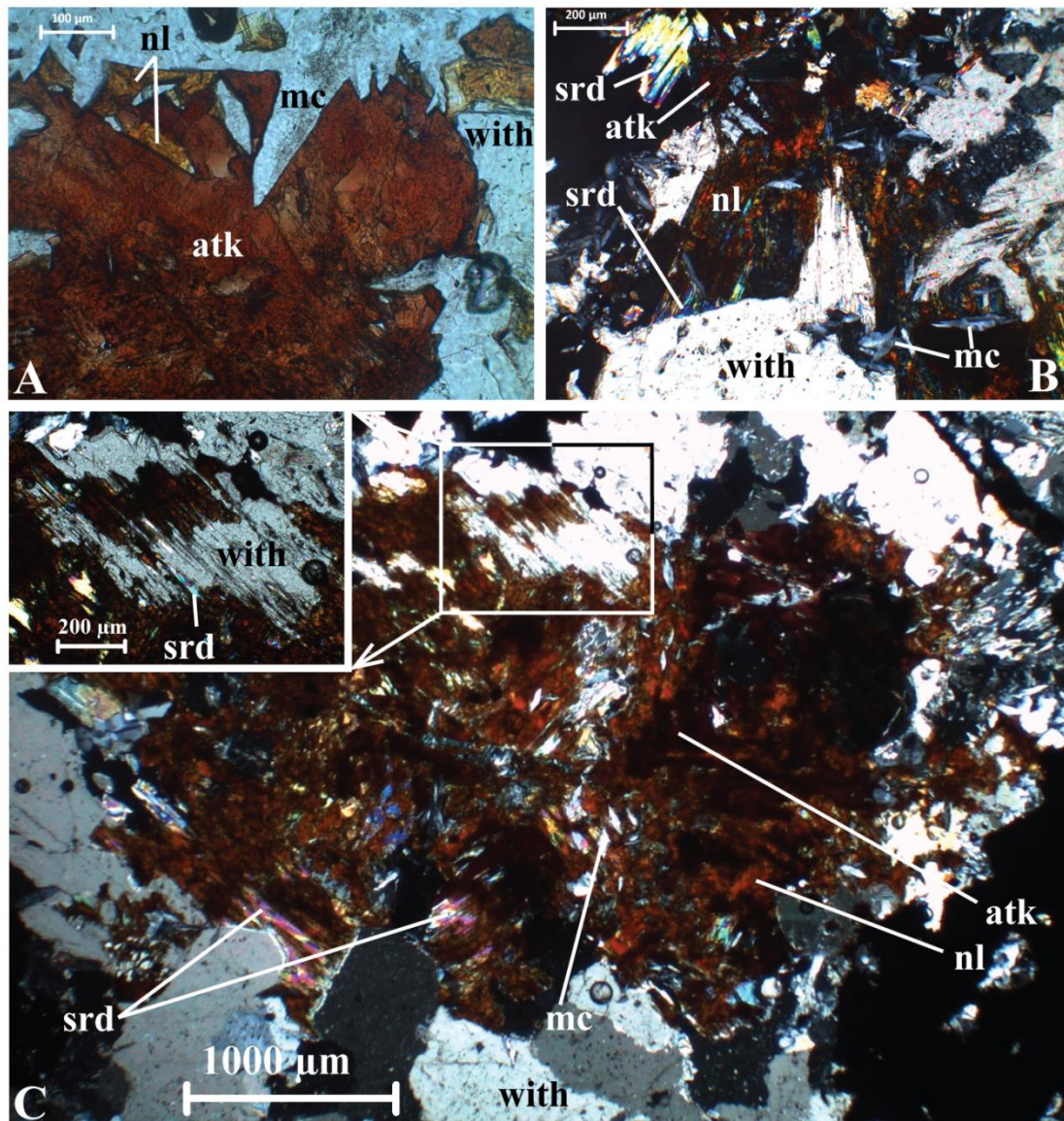


Figure 3.4: Photomicrographs of vug-fill minerals in the lower portion of drill core SLT-015 (all from sample 15-23). **A.** Coarse-grained (approx. 200 μm on average) tokyoite in the centre of the vug surrounded by witherite and microcline adularia. Minor noélbensonite is also present (PPL). **B.** Minor subhedral sérandite adjacent to tokyoite and noélbensonite. Pseudomorphous replacement of sérandite by witherite is shown in the lower centre of the image (XPL). **C.** Aggregated noélbensonite and arsenotokyoite surrounded by euhedral, coarse-grained (up to 1000 μm) witherite. The lower part of the image shows sérandite replaced by tokyoite and noélbensonite. Inset shows pseudomorphous witherite after sérandite with minor relict sérandite laths. Fine-grained (<100 μm) adularia are randomly distributed within the vug (XPL).

Witherite, in Figure 3.4.B and the inset in Figure 3.4.C, has replaced a cleavage-bearing mineral and small laths of sérandite occur parallel to the relict cleavage planes. This is suggestive of pseudomorphous replacement of sérandite by witherite. Figure 3.4.B and C also suggest the replacement of sérandite by noélbensonite and arsenotokyoite with relict sérandite remaining as well as relict cleavage planes in the noélbensonite and arsenotokyoite.

Table 3.2: Average end-member composition of sérandite in drill core SLT-015.

Oxide wt. %	n = 13	Std. Dev.
SiO ₂	49.96	0.37
Al ₂ O ₃	0.01	0.01
FeO	0.03	0.03
MnO	36.09	0.47
CaO	1.95	0.27
Na ₂ O	8.94	0.18
K ₂ O	0.02	0.01
H ₂ O*	2.49	0.01
Total	99.49	
Calculated on the basis of 8.5 O		
Si	3.01	
Al	0.00	
Fe	0.00	
Mn	1.84	
Ca	0.13	
Na	1.04	
K	0.00	

*Calculated according to sérandite mineral formula

Similar to sérandite-pectolite from the Bruce locality described by Moore *et al.* (2011), the sérandite end-member is far more common in the SLT-015 drill core than the calcic pectolite end-member but intermediate compositions also occur (Figure 3.5). The lower portion of the stratigraphy contains no pectolite. Instead sérandite occurs as fine (<100 µm) relict laths or as blocky grains with serrated edges (Figure 3.4.B – top left corner).

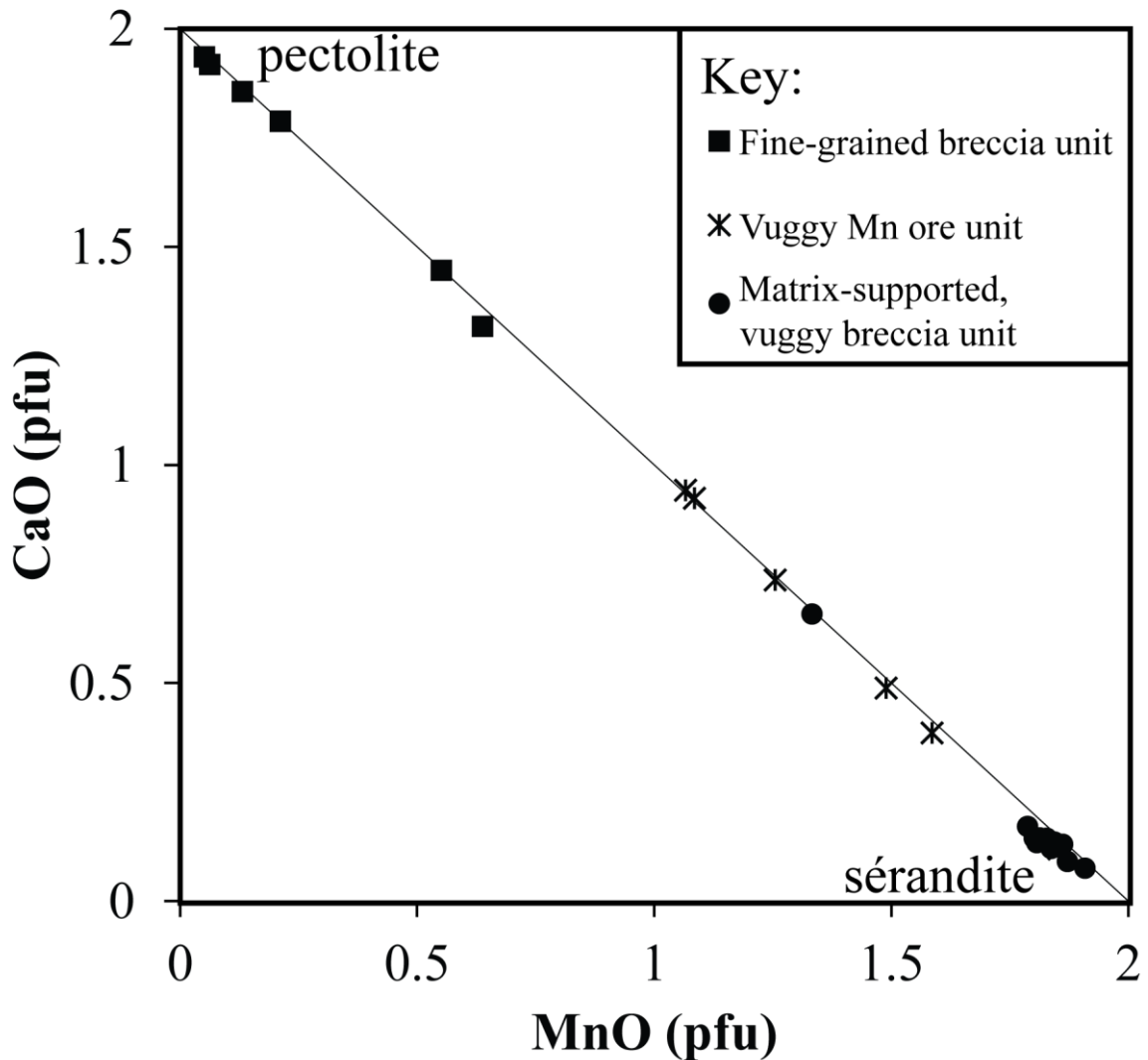


Figure 3.5: Per formula unit binary plot of Ca vs. Mn demonstrating the compositional variation of sérandite-pectolite in drill core SLT-015.

The matrix in this unit consists of fine-grained, manganese-bearing hematite and, to a lesser extent, aluminium-bearing braunite. Hydrous iron oxide phases are also present. This matrix is mostly finely laminated but botryoidal textures also exist as well as microscopic hematite concretions which are enveloped by a manganese-bearing, hydrous iron oxide. The backscattered electron image in Figure 3.6 illustrates the slight difference in iron concentration between the inner and outer zones of the concretions which cannot be seen by reflected-light microscopy. The outer zones also contain manganese in some instances.

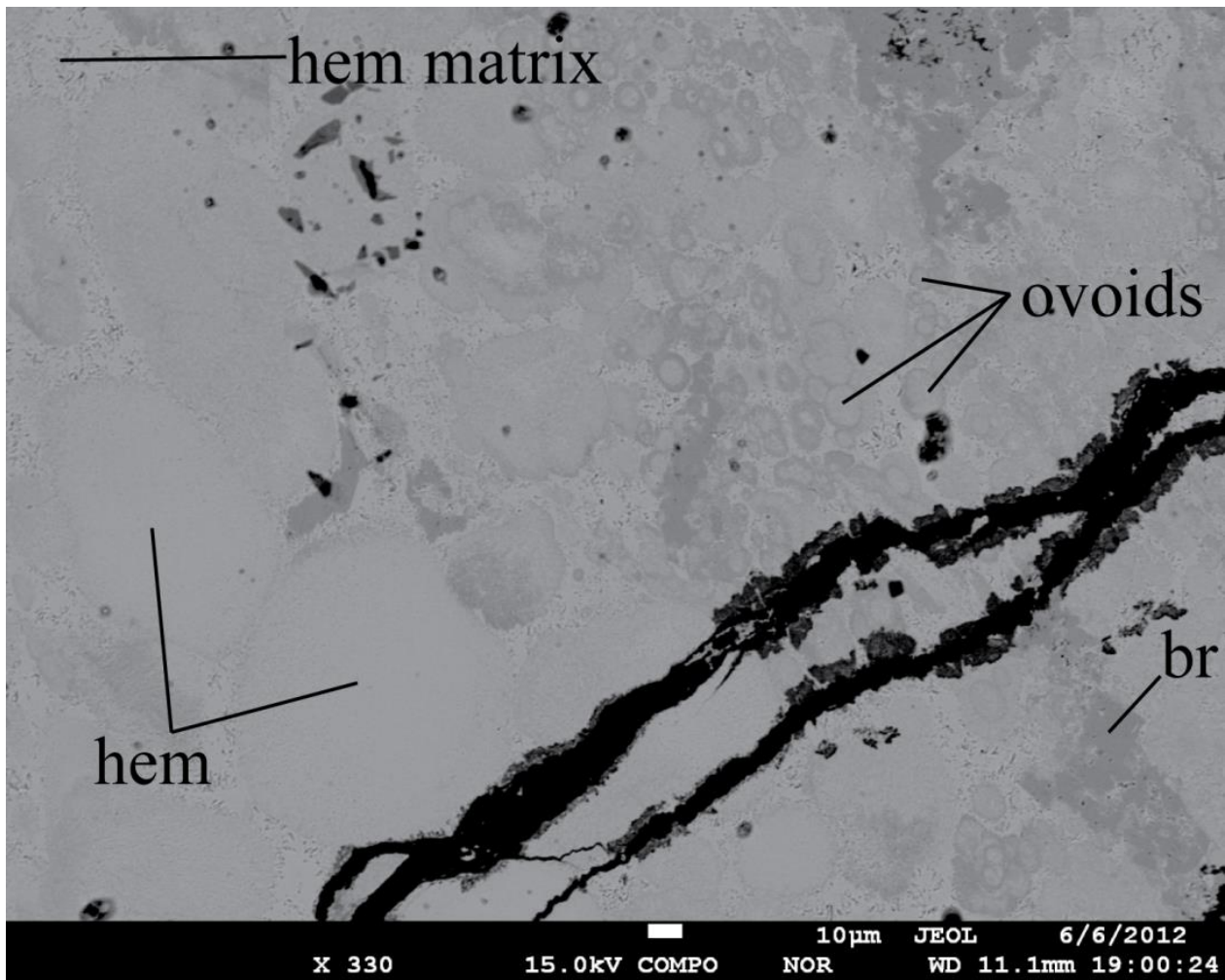


Figure 3.6: Backscattered electron image of hematite concretions in the matrix of sample 15-23 in drill core SLT-015. Interstices between concretions consist of cryptoplaty hematite.

Electron microprobe analyses of hematite across the entire sampled section of drill core SLT-015 reveals varying compositions, particularly for Mn_2O_3 and Fe_2O_3 which tend to substitute for one another in the hematite structure. Table 3.3 illustrates this variation in Mn_2O_3 and Fe_2O_3 . The average analysis also reflects the composition of manganese-bearing hematite. Hematite compositional changes seem to occur at random within the stratigraphy.

Table 3.3: Average microprobe analyses of hematite in drill core SLT-015.

Oxide wt. %	n = 14	Std. Dev.	Range
TiO ₂	0.10	0.08	<0.016- 0.21
Al ₂ O ₃	0.48	0.54	0.02 - 1.72
SiO ₂	0.57	0.10	0.43 - 0.74
Fe ₂ O ₃	94.45	2.19	90.35 - 97.27
Mn ₂ O ₃	4.13	2.03	0.12 - 6.86
Cr ₂ O ₃	0.01	0.02	<0.010 - 0.04
Total	99.75	0.99	98.14 - 100.64
Cations calculated on the basis of 3 O:			
Ti	0.00		
Al	0.02		
Si	0.02		
Fe	1.88		
Mn	0.08		
Cr	0.00		

3.2.4. Aegirine-augite-bearing, clast-supported breccia

The matrix-supported breccia grades back into clast-supported breccia at a depth of around 95 m (Figure 3.7). Some petrographic distinctions exist, however, between this clast-supported breccia and that at the base. Chert is still present but individual, coarse-grained quartz is also present. These coarse quartz grains are anhedral to subhedral with some displaying growth zones. The matrix consists of platy hematite and hydrous iron oxide exhibiting various colloform textures.

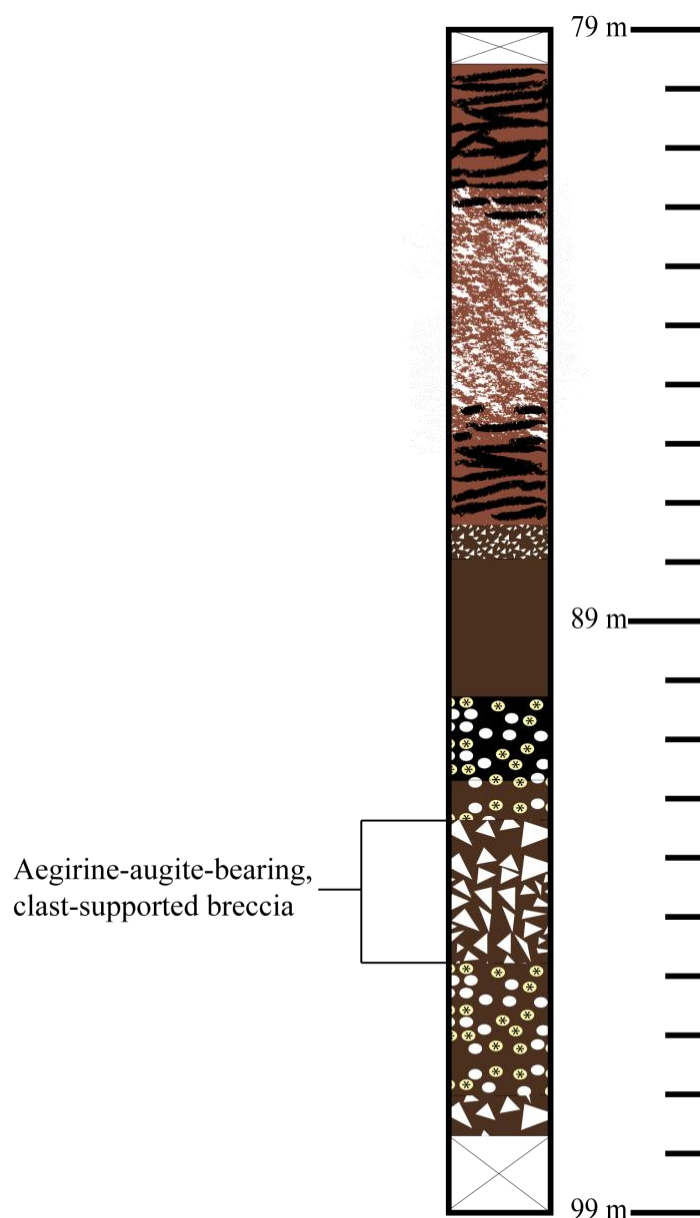


Figure 3.7: Stratigraphic position of the aegirine-augite-bearing, clast-supported breccia unit in SLT-015.

A mineral appears toward the top of this unit that is not present in the clast-supported breccia at the base. It mainly occurs as extremely fine-grained aggregates in small vugs and as fine-grained acicular, aggregated grains growing outwards from quartz-filled vugs (Figure 3.8.A). Semi quantitative analysis using microprobe wavelength dispersive spectroscopy (WDS) reveals that this mineral consists of Na, Fe, Si and Ca as well as minor Al (Figure 3.8.B) and is most likely to be a member of the aegirine-augite solid solution series.

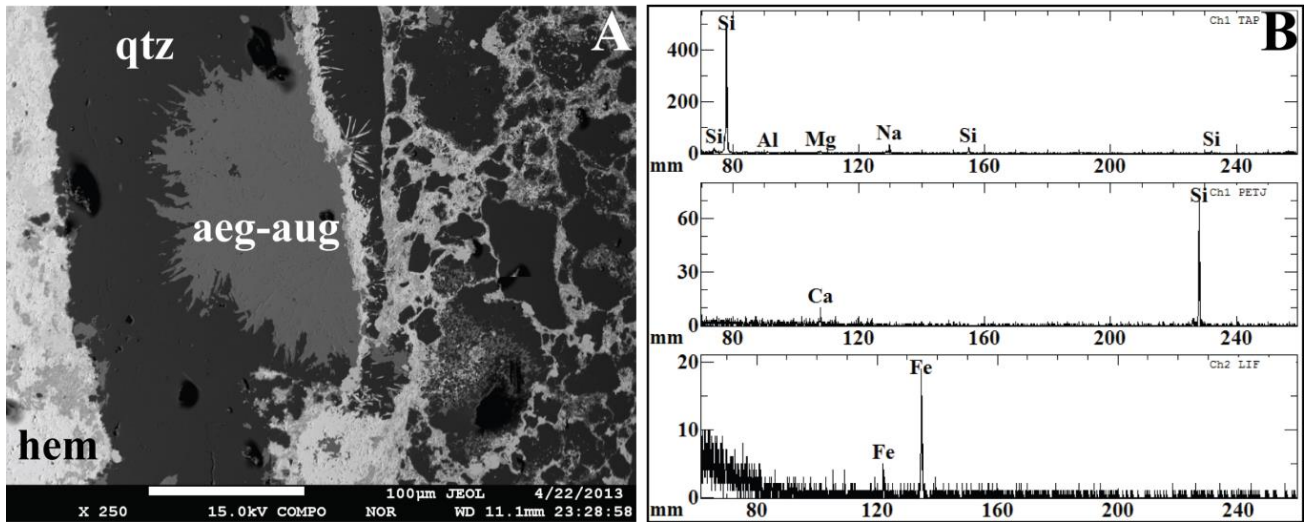


Figure 3.8: Aegirine-augite in the upper clast-supported chert breccia unit in drill core SLT-015. **A.** Backscatter electron image of acicular, aggregated aegirine-augite growing inward from the boundary of a quartz-dominated vug (sample 15-16). **B.** WDS scan of aegirine-augite in drill core SLT-015 (sample 15-17).

3.2.5. *Aegirine-rich, matrix-supported breccia*

At a depth of approximately 92.5 m the clast-supported breccia grades into matrix-supported breccia where vuggy textures occur along with associated vug-filling minerals (Figure 3.9). Chert is absent in this zone but coarse-grained quartz is present in vugs. Many of these vugs also contain a variety of other minerals. Aegirine lines the boundaries of most vugs, with coarse quartz generally forming the inner core. The presence of aegirine in these rocks is of interest as the mineral seems to be omnipresent in ores and surrounding country rock throughout the KMF and PMF. Aegirine is described from the Bruce iron ore mine by Moore *et al.* (2011) where it occurs in proximity to void fillings. Aegirine has also been reported from the manganese ore bodies of the Wessels mine in the KMF by Dixon (1989). Tsikos and Moore (2005) further describe aegirine in banded iron-formation bordering manganese deposits of the Hotazel Formation in the KMF.

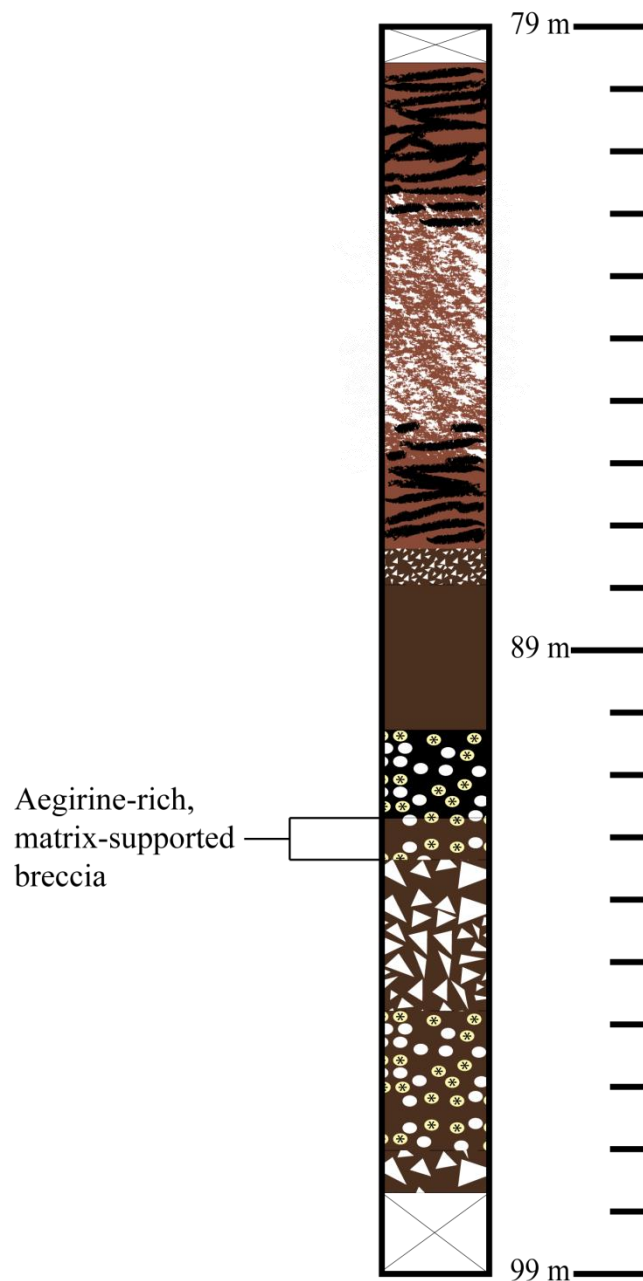


Figure 3.9: Stratigraphic position of the aegirine-rich, matrix-supported breccia unit in SLT-015.

Microprobe analyses of aegirine from drill core SLT-015 are presented in Table 3.4. Aegirine compositions from Wessels Mine in the north are very similar to that analysed in drill core SLT-015. In aegirine-rich samples, the matrix contains approximately 10 wt. % sodium (Table 3.4). Given the amount of silicon in this matrix (ca. 36 wt. %), almost all of the sodium can be accounted for by 68% modal abundance of aegirine.

Table 3.4: Average aegirine composition of 19 microprobe analyses in drill core SLT-015 as well as an analysis of aegirine from Wessels Mine and an analysis of the matrix in sample 15-15N. The matrix was analysed as a mixed analysis of fine-grained material using a microprobe beam diameter of 10 μm .

Oxide wt. %	n = 19	Std. Dev.	Wessels ^a	15-15N matrix
SiO ₂	52.24	0.34	52.36	36.57
Al ₂ O ₃	0.53	0.38	0.04	0.33
Fe ₂ O ₃ *	30.54	1.61	29.92	49.36
MnO*	1.04	0.59	n.d	1.37
Mn ₂ O ₃	n.d		2.21	n.d
MgO	0.26	0.46	0.24	0.15
CaO	0.28	0.45	0.46	0.13
Na ₂ O	13.97	0.40	14.00	10.82
K ₂ O	0.04	0.05	n.d	0.05
Total	98.86	0.58	99.19	98.80
Calculated on the basis of 6 O				
Si	2.02		2.02	
Al	0.02		0.00	
Fe	0.89		0.87	
Mn	0.03		0.07	
Mg	0.02		0.01	
Ca	0.01		0.02	
Na	1.05		1.05	
K	0.00		-	

Abbreviations: a - microprobe analysis of aegirine by Dixon (1989); * Total Fe as Fe₂O₃, total Mn as MnO

The aegirine in drill core SLT-015 generally occurs as fine-grained (<50 μm) aggregates at the vug boundary with blades growing out from fine aggregations toward the centre of the vug as in Figure 3.10.A. Some vugs contain varying amounts of microcline, aegirine and sérandite as the main mineral constituents. Figure 3.10.B shows microcline (adularia) and radial aggregates of sérandite in an irregular-shaped vug. The microcline forms the outer zone of the vug with sérandite in the centre. The majority of the sérandite found in SLT-015 occurs as radial aggregates as displayed in Figure 3.10.C. Here a subhedral quartz grain appears to have undergone pseudomorphous replacement by sérandite. Smaller vugs can be filled almost entirely by one mineral such as in Figure 3.10.D where aegirine is the dominant mineral with only minor quartz. Albite is present in this unit showing various habits. The euhedral albite in Figure 3.10.E shows typical Carlsbad twinning as well as small inclusions of sérandite; the inclusions suggesting crystallization of albite after sérandite. Coarse-grained (average size of 200 μm), anhedral albite also occurs in this unit, with single grains filling available, small voids and taking on the shape of the void.

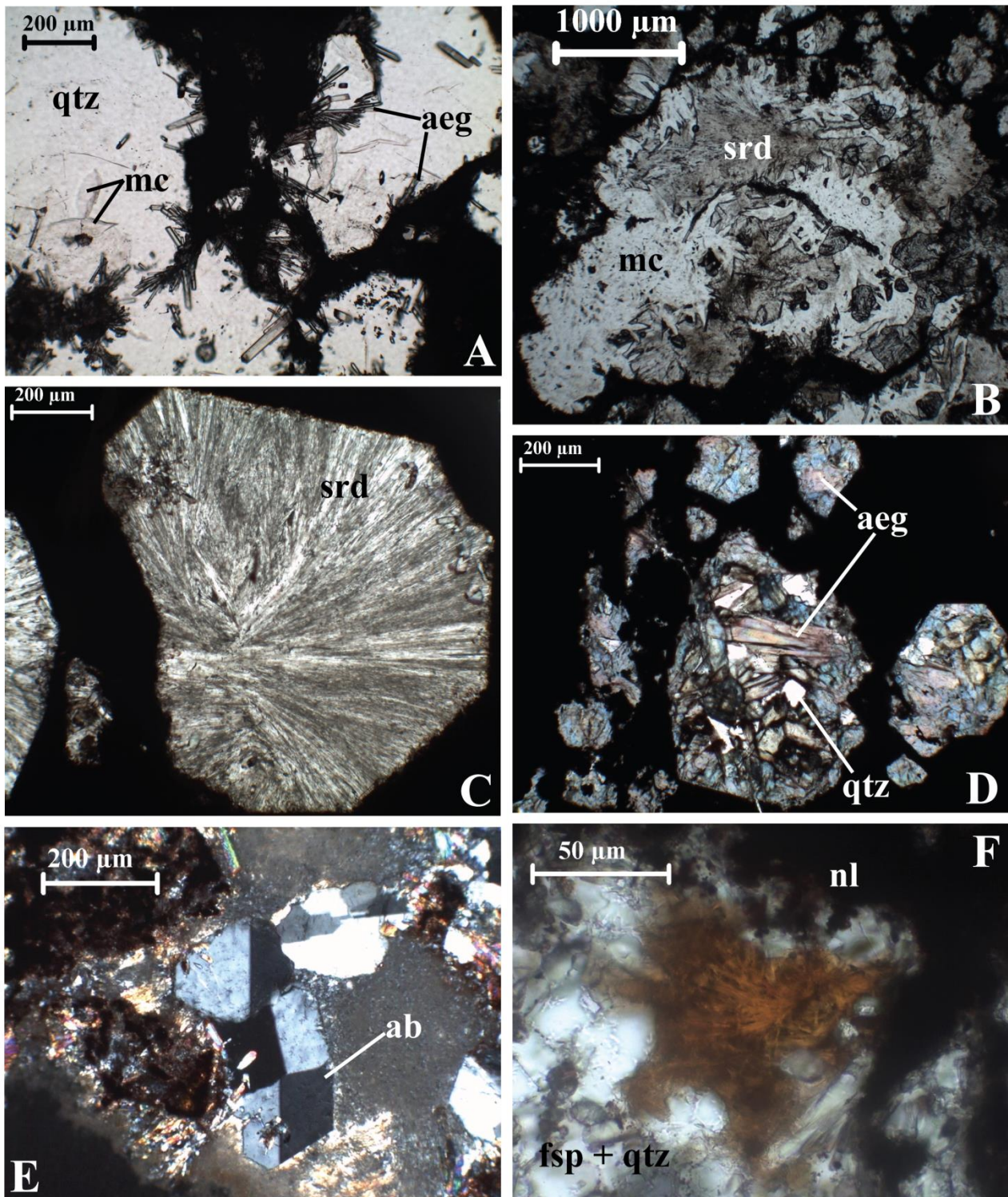


Figure 3.10: Photomicrographs of some textures in matrix-supported breccia overlying the uppermost clast-supported breccia in drill core SLT-015. **A.** Blades of aegirine growing inward from vug boundaries. Microcline adularia and quartz is also present (PPL, sample 15-15Q). **B.** Vug consisting of microcline toward the edges and sérandite toward the centre. (PPL, sample 15-15Q). **C.** Pseudomorphous sérandite after quartz (PPL, sample 15-15Q). **D.** Aegirine filling smaller vugs with minor quartz. Also shows the distinct pale brown to blue pleochroism typical of aegirine (PPL, sample 15-15Q). **E.** Albite showing Carlsbad twins. (XPL, sample 15-15Q). **F.** Aggregated needles of noélsenite as found toward the middle and top of the stratigraphy in drill core SLT-015 (PPL, sample 15-15Q).

Table 3.5 shows average analyses for the two types of feldspar in drill core SLT-015. Both feldspar species in this drill core represent the nearly pure sodic and potassic end-members.

Table 3.5: Average microprobe analyses of albite and microcline in drill core SLT-015.

Oxide wt. %	Albite		Microcline	
	n = 17	Std. dev.	n = 11	Std. Dev.
SiO ₂	68.94	0.44	64.10	0.54
Al ₂ O ₃	19.31	0.13	18.89	0.38
Fe ₂ O ₃	n.d		0.02	0.02
FeO	0.01	0.03	n.d	
Mn ₂ O ₃	n.d		0.06	0.10
MnO	0.02	0.02	n.d	
BaO	n.d		0.01	0.01
SrO	n.d		0.32	0.46
CaO	0.02	0.01	0.00	0.01
Na ₂ O	11.72	0.18	0.07	0.04
K ₂ O	0.01	0.01	16.25	0.77
Total	100.04	0.62	99.61	0.83
Cations calculated on the basis of 8 O:				
Si	3.01		2.98	
Al	0.99		1.03	
Fe	0.00		0.00	
Mn	0.00		0.00	
Ba			0.00	
Sr			0.01	
Ca	0.00		0.00	
Na	0.99		0.01	
K	0.00		0.96	

Noélbensonite is also present in this unit (Figure 3.10.F). It predominantly occurs as very fine-grained (< 20 µm) aggregated needles. This is the highest unit in which one finds this mineral in drill core SLT-015. Table 3.6 presents the average composition of noélbensonite in SLT-015. Compositional variations are not observed between the generally coarser-grained, blocky noélbensonite in the lower units and the finer-grained aggregated needles.

Table 3.6: Average of 12 microprobe analyses of noélbensonite in SLT-015.

Oxide wt. %	n = 12	Std. Dev.
SiO ₂	27.53	0.58
Al ₂ O ₃	0.22	0.03
Mn ₂ O ₃	35.21	0.93
BaO	26.03	1.66
CaO	1.21	0.60
SrO	2.02	0.56
H ₂ O*	8.12	0.10
Total	100.33	0.47
Cations calculated on the basis of 8 O:		
Si	2.03	
Al	0.02	
Mn	1.98	
Ba	0.75	
Ca	0.10	
Sr	0.09	
*Calculated according to noélbensonite mineral formula;		

This unit, in places, also shows highly irregular vugs which contain single, coarse quartz grains as shown in Figure 3.11. This suggests that, upon deposition of silicon to form quartz, the quartz grain adopted the shape of the vugs. It is likely that these irregular vugs are the result of dissolution of chert and redeposition of silicon as coarse-grained quartz.

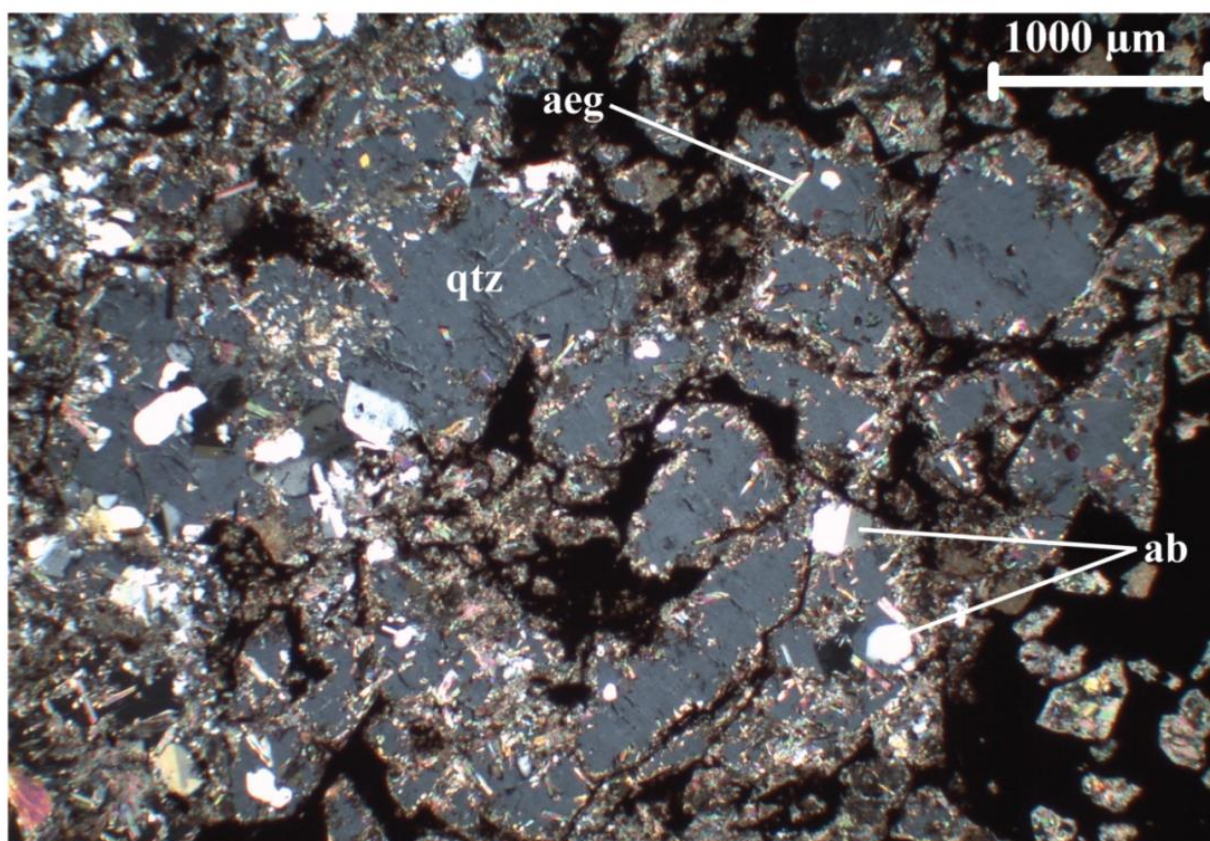


Figure 3.11: Photomicrograph of quartz occupying a highly irregular vug. Albite and aegirine are also present (XPL, sample 15-15Q).

The iron-rich nature of the matrix in this unit is evident in Figure 3.12. These elemental distribution maps indicate relative abundances of Al, Na, Fe and Si. Manganese and potassium were also analysed but revealed little. It is thus evident that the matrix, in the case of this unit, consists primarily of Fe, Na and Si. The map for Si shows some fine-grained quartz in the bottom left hand corner. The maps for Fe and Na show that two compositions of matrix exist in this case: one that is Na-bearing yet still contains Fe and one that is Fe-rich with little to no Na. The Na-bearing matrix shows uniform distribution of both Na and Fe. Small Na-bearing grains also exist which are also evident in the Si and Al maps. The even distribution of Na and Fe in the Na-bearing matrix suggests one of two possibilities: firstly that the matrix consists of evenly distributed, equigranular, cryptocrystalline mineral phases that are composed of Fe and Na or, secondly, that the matrix is an amorphous mixture of predominantly Fe and Na. The first possibility is favoured with the matrix most likely to be composed of aegirine (considering, also, the presence of Si in the matrix) and hematite.

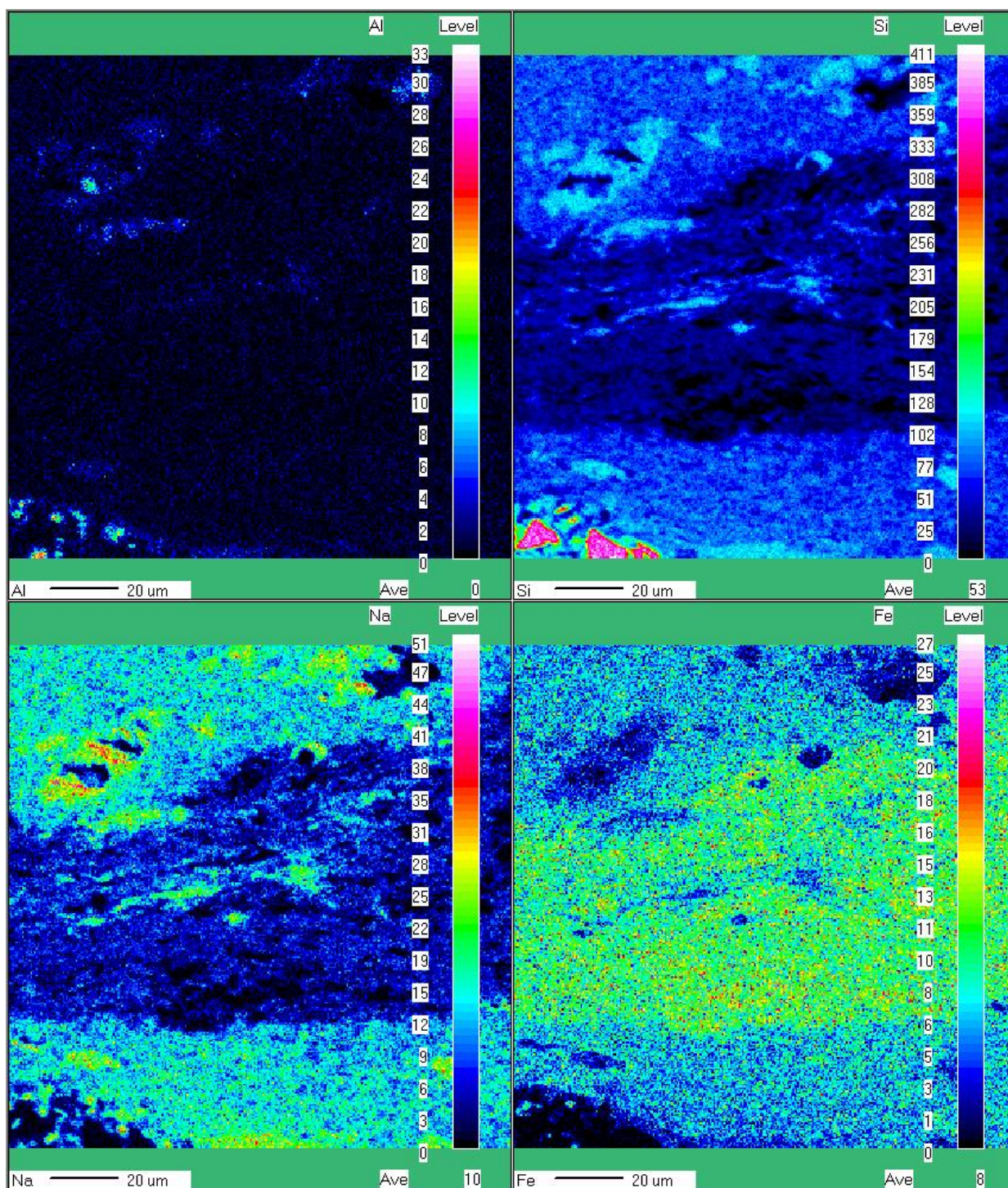


Figure 3.12: Relative concentrations in electron microprobe elemental distribution maps for Al, Si, Na and Fe in a portion of the matrix from sample 15-150 in drill core SLT-015. Vugs are also present, accounting for anomalously higher relative concentrations in some elements. Scales represent counts per second.

3.2.6. Vuggy manganese ore

Overlying the aegirine-rich, matrix-supported breccia unit is approximately one meter of extremely vuggy manganese ore (Figure 3.13). In this unit braunite and hematite are the dominant ore minerals, with vugs filled with various silicate, sulphate and carbonate phases.

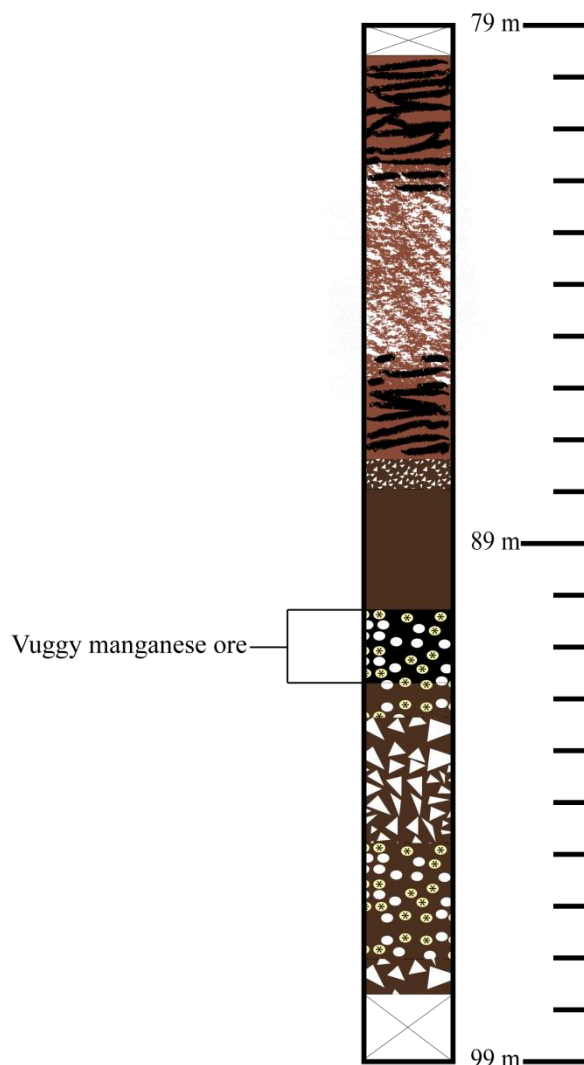


Figure 3.13: Stratigraphic position of the vuggy manganese ore unit in SLT-015.

The dominant silicate phases in this unit are sérandite, feldspar and quartz. These phases are disseminated throughout the unit filling the abundant voids. In some cases witherite and albite occur as aggregated masses (Figure 3.14.A). The witherite tends to be more coarse-grained than the albite.

Some vugs and veins contain small amounts of barite. Figure 3.14.B shows that, in places, barite can contain inclusions of acicular to columnar strontianite. Extremely fine-grained strontianite has also been identified replacing witherite along grain boundaries. Sérandite also occurs in vugs and as a replacement of quartz. In Figure 3.14.C, sérandite is replacing quartz but some relict quartz still remains. Aegirine occurs in some vugs but it is scarce in this unit. The aegirine occurs as coarse-grained (up to 1000 μm) vug-fills as shown in Figure 3.14.D. One sample in this unit contains coarse-grained, angular vugs that have cores of coarse-grained (up to 2 mm) calcite and rims of finer-grained albite ($\sim 500 \mu\text{m}$ on average) in a matrix of crystalline braunite (Figure 3.14.E). Here, albite and natrolite can also be found as the only minerals occupying smaller vugs. Figure 3.14.F illustrates the hand specimen of the texture described in Figure 3.14.E. This is another case where, in hand-specimen, the angular fragments appear clastic but show petrographic textures indicative of vug-filling.

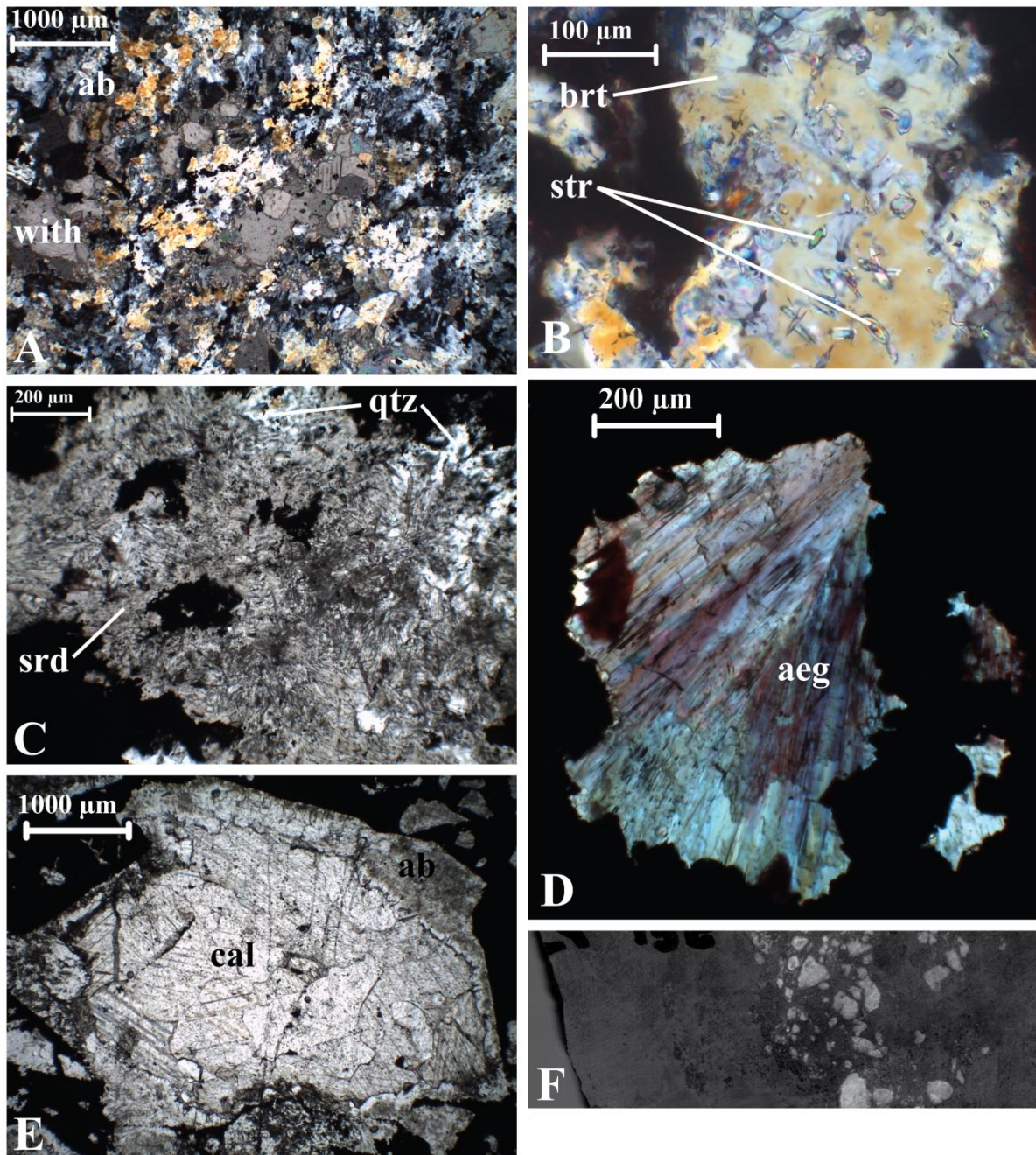


Figure 3.14: Photomicrographs of the gangue phases in the extremely vuggy crystalline manganese unit in SLT-015. **A.** Aggregated masses of albite and witherite as voids fillings (XPL, sample 15-15G, slightly thick section). **B.** Coarse-grained barite with strontianite inclusions (XPL, sample 15-15I). **C.** Matted sérandite replacing quartz with some relict quartz still present (PPL, sample 15-15J). **D.** Coarse-grained aegirine filling voids in a predominantly braunite-hematite matrix (PPL, sample 15-15H). **E.** Zoned vugs with cores of coarse-grained calcite and rims of albite (PPL, sample 15-15E). **F.** Sample 15-15E in hand specimen – note the clastic appearance of the gangue phases.

The matrix in this unit predominantly consists of braunite, partridgeite and hematite. The braunite and partridgeite occur together and are typically crystalline with grain size ranging from

microcrystalline to approximately 200µm. The hematite also ranges in size (up to ~ 200 µm) and most commonly displays a platy habit. The matrix is highly vuggy with empty vugs in the interstices between hematite plates as well as between and within braunite and partridgeite grains. Table 3.7 shows the average analyses for braunite and partridgeite in drill core SLT-015. The partridgeite contains some SiO₂ and CaO. This is most likely a result of the presence of small amounts of braunite inclusions within the partridgeite. Fe₂O₃ concentrations are similar in both braunite and partridgeite.

Table 3.7: Average compositions of braunite and partridgeite in drill core SLT-015.

Braunite				Partridgeite		
Oxide wt. %	n = 25	Std. Dev.	Range	n = 6	Std. Dev.	Range
SiO ₂	9.69	0.74	7.72 - 10.68	2.25	0.56	1.47 - 3.22
Al ₂ O ₃	0.71	0.40	0.17 - 1.7	0.66	0.13	0.47 - 0.86
Fe ₂ O ₃	2.97	1.82	0.16 - 5.66	3.01	0.45	2.46 - 3.67
Mn ₂ O ₃	74.81	2.85	70.45 - 79.42	95.57	0.82	94.89 - 97.00
MnO*	9.38	0.85	7.50 - 10.50	n.c	n.c	
MgO	0.08	0.04	<0.006 - 0.17	0.05	0.01	0.03 - 0.07
CaO	1.51	0.43	0.46 - 2.04	0.31	0.09	0.19 - 0.47
SrO	0.01	0.02	<0.007 - 0.07	n.d	n.d	
Total	99.17	0.74	98.11 - 100.69	101.85	0.77	100.62 - 102.68

Cations calculate on the basis of 12 O for braunite and 3 O for partridgeite:

Si	0.98	0.06
Al	0.08	0.02
Fe	0.23	0.06
Mn ³⁺	5.74	1.84
Mn ²⁺	0.80	
Mg	0.01	0.00
Ca	0.16	0.01
Sr	0.00	

Abbreviations: n - number of analyses; n.c - not calculated; n.d - not determined

* Mn²⁺ - Mn³⁺ charge balance calculated based on 12 O

In some instances, a textural relationship is observed between the partridgeite and braunite. Figure 3.15.A shows just such a relationship whereby manganese concretions form concentric, compositionally distinct zones. The inner and outer zones consist of partridgeite whereas the middle zone consists of braunite. These localised concretions occur in a matrix of cryptoplaty hematite adjacent to massive, crystalline braunite and partridgeite (Figure 3.15.B). A typical texture found in this unit is shown in Figure 3.15.C where vugs are lined by euhedral braunite crystals. In this case, a

ehedral braunite grain has been incompletely replaced by sérandite leaving a relict braunite skeleton. However, in one case, where vugs consist of calcite and albite as described previously, some vug-fills are either partially or completely replaced by fine-grained braunite as shown in Figure 3.15.D. The entire replacement process is seen in this image, from unaffected gangue phases to partial replacement and finally to complete replacement of gangue vugs-fills by braunite. This suggests manganese mobilization after deposition of the calcite and albite.

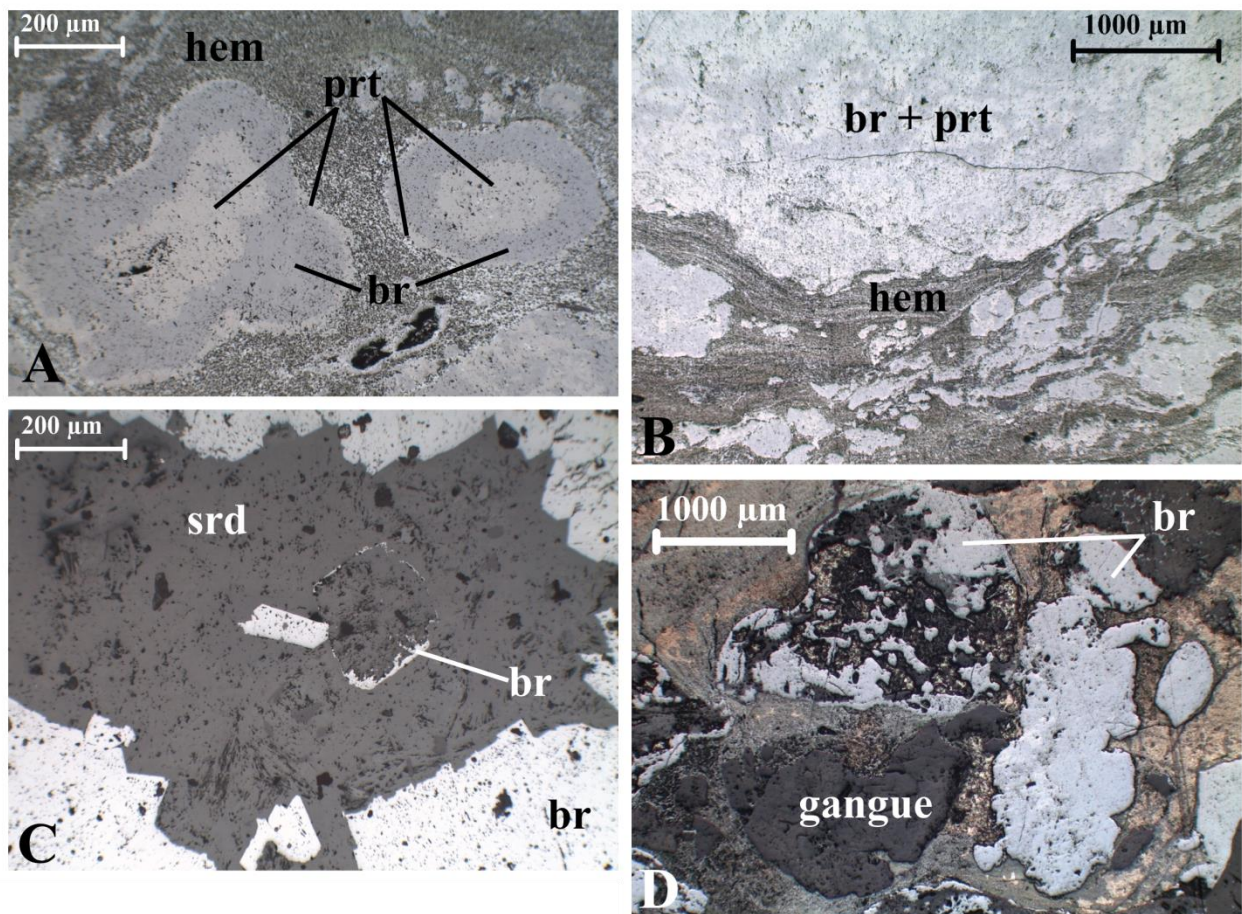


Figure 3.15: Reflected-light photomicrographs of textures in the matrix of the extremely vuggy crystalline manganese unit in SLT-015. **A.** Zoned manganese concretions with inner and outer zones consisting of partridgeite and a middle zone of braunite. The surrounding matrix consists of cryptoplaty hematite (sample 15-15E). **B.** Massive braunite and partridgeite adjacent to concretions of braunite and partridgeite in a cryptoplaty hematite matrix (sample 15-15E). **C.** Euhedral braunite lining a sérandite-filled vug (sample 15-15J). **D.** Fine-grained braunite partially and completely replacing calcite-albite-filled vugs (sample 15-15E).

3.2.7. Massive ferromanganiferous ore unit

At hand-specimen scale, the vuggy manganese ore unit grades upwards into massive ferromanganiferous ore with very few vugs or vug-filling minerals (Figure 16). However, reflected light microscopy reveals that this unit is laminated, in places, at a microscopic scale and that vugs are still present.

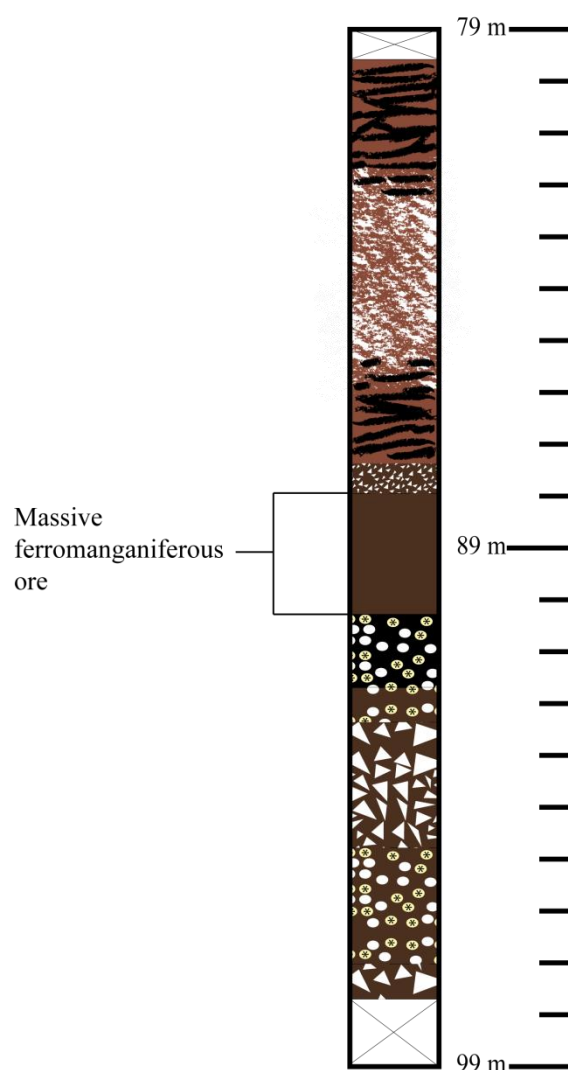


Figure 3.16: Stratigraphic position of the massive ferromanganiferous ore unit in drill core SLT-015.

Figure 3.17 shows the major textural features as seen in this unit. Parts of this unit show coarse-grained crystalline hematite as is displayed in Figure 3.17.A. Other portions may show colloform

textured, cryptoplaty hematite such as that displayed in Figure 3.17.B. However, the most common textural feature in this unit is that of extremely finely laminated cryptoplaty hematite and hollandite. Figure 3.17.C shows monomineralic clasts of braunite in a matrix of laminated cryptoplaty hematite and hollandite (grain size $<10\text{ }\mu\text{m}$), where laterally discontinuous laminae have wrapped around the clasts. Microplaty hematite appears to be replacing the braunite-rich clasts in this case. The contrasting colours in the matrix in Figure 3.17.C can be attributed to a difference in the amount of space between grains, with darker areas having a greater amount than lighter areas. Parts of this unit show similar features to the unit stratigraphically below, with concretions or clasts of braunite and partridgeite in a matrix of massive cryptoplaty hematite as shown in Figure 3.17.D. Although some of these concretions show phase zonation, the majority do not.

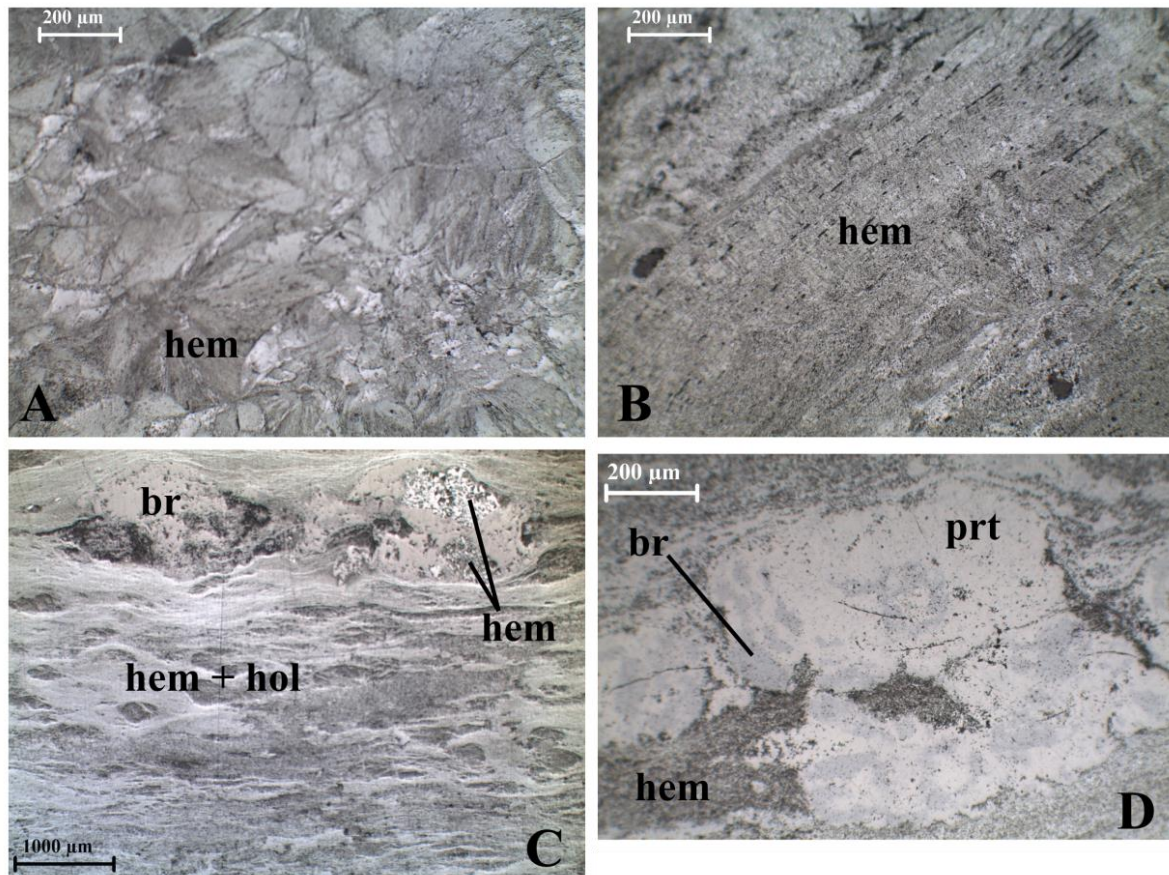


Figure 3.17: Reflected-light photomicrographs of the matrix in the so-called massive ferromanganiferous ore unit. **A.** Massive crystalline hematite (sample 15-15A). **B.** Colloform-textured cryptoplaty hematite (sample 15-15A). **C.** Laminated cryptoplaty hematite in sample 15-13. Laterally discontinuous laminae wrapped around braunite-rich (with microplaty hematite) clasts. **D.** Clasts or concretions consisting of braunite and partridgeite in massive cryptoplaty hematite matrix (sample 15-15B).

Hollandite is a Ba-Mn oxide that is generally associated with supergene alteration but has also been found in contact metamorphic manganese ores (Anthony *et al.*, 2003). Table 3.8 shows 5 microprobe analyses of this mineral in drill core SLT-015. The quality of the data shown in this table is compromised by the extremely fine-grained size of available material. The presence of Na₂O, K₂O, SiO₂ and CaO may be as a result of mixed analyses. However, it is likely that the Na₂O is part of the hollandite structure. This hollandite also contains around 4 wt. % Fe₂O₃.

Table 3.8: Five analyses of hollandite in sample 15-13 from drill core SLT-015.

Oxide wt. %	Hollandite					Average	Std. Dev
	15-13	15-13	15-13	15-13	15-13		
SiO ₂	0.35	0.24	0.29	0.65	0.37	0.38	0.16
Al ₂ O ₃	0.44	0.55	0.54	0.77	0.47	0.55	0.13
MnO ₂ *	80.27	76.56	77.47	77.07	77.89	77.85	1.44
Fe ₂ O ₃	4.01	3.94	4.37	4.45	4.89	4.33	0.38
CaO	0.54	0.40	0.41	0.42	0.42	0.44	0.06
BaO	14.93	14.89	15.70	15.15	14.65	15.06	0.40
K ₂ O	0.67	0.47	0.40	0.57	0.56	0.53	0.10
Na ₂ O	0.98	1.03	1.15	1.32	0.92	1.08	0.16
Total	102.19	98.09	100.31	100.40	100.15	100.23	1.46
Cations calculated according to 16 O:							
Si	0.05	0.03	0.04	0.09	0.05	0.05	
Al	0.07	0.09	0.08	0.12	0.07	0.09	
Mn	7.11	7.10	7.05	6.97	7.05	7.06	
Fe	0.39	0.40	0.43	0.44	0.48	0.43	
Ca	0.07	0.06	0.06	0.06	0.06	0.06	
Ba	0.75	0.78	0.81	0.78	0.75	0.77	
K	0.11	0.08	0.07	0.10	0.09	0.09	
Na	0.24	0.27	0.29	0.33	0.23	0.27	

*All Mn reported as Mn⁴⁺

The distribution of hollandite in this unit is illustrated by the distribution of barium in the microprobe element distribution maps shown in Figure 3.18.A. This figure shows that the matrix of this unit is predominantly composed of hollandite (Ba and Mn maps) and hematite (Fe map). K is also present in the matrix as is Na and Al. Some silicates show replacement by hollandite. The presence of hollandite and hematite is also shown in the XRD spectrum in Figure 3.18.B. A lesser amount of braunite is also expressed in the XRD spectrum as is to be expected with braunite-rich clasts being present in this unit.

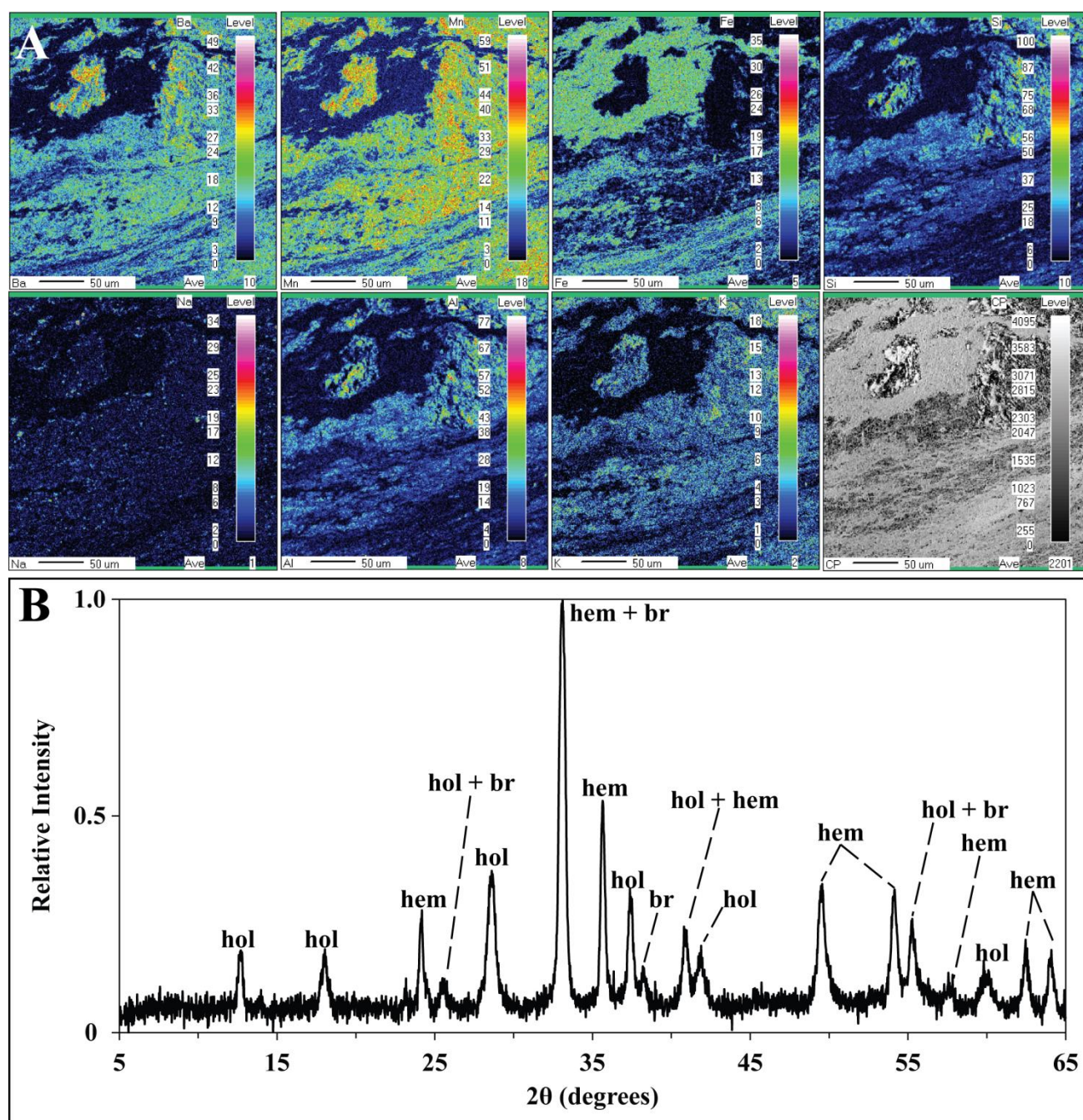


Figure 3.18: Matrix composition in the massive ferromanganese ore unit in drill core SLT-015. **A.** Various element distribution maps attained by microprobe of the matrix (sample 15-13). **B.** Bulk rock powder XRD spectrum of sample 15-13.

3.2.8. Fine-grained breccia

An approximately 60 cm thick unit of fine-grained breccia overlies the massive ferromanganiferous unit. This presents yet another case in which clastic textures are observed at hand specimen scale but petrographic evidence indicates post-depositional processes. Some well-rounded, essentially monomineralic (either hematite or braunite) clasts are present. However, polymineralic vugs are dominant. The stratigraphic position of this unit is shown in Figure 3.19.

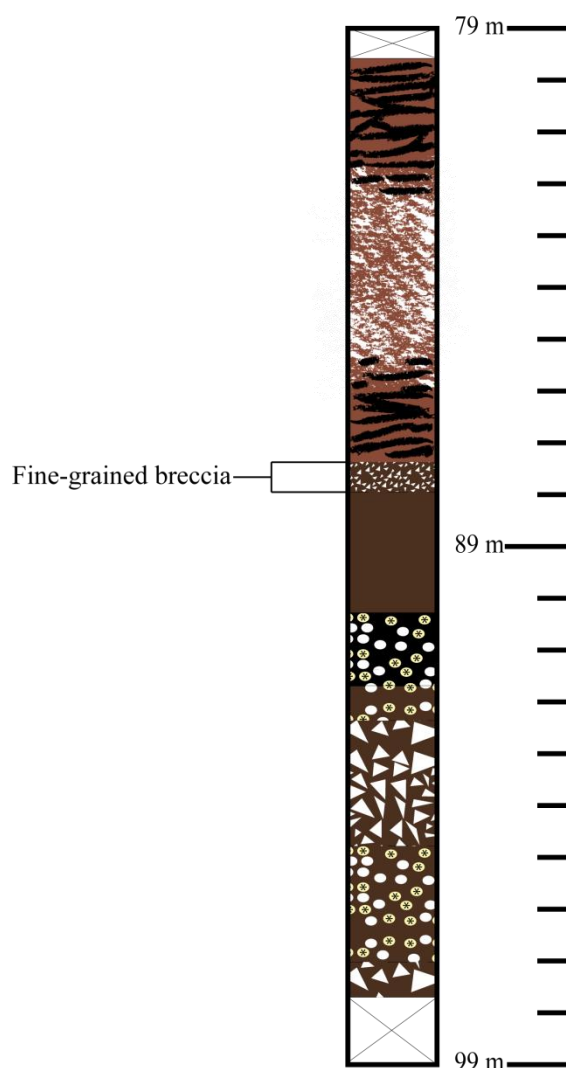


Figure 3.19: Stratigraphic position of the fine-grained breccia unit in SLT-015.

Quartz is one of the major constituents of the vugs, where it generally occurs as the central core. The quartz can display brittle fracturing as is evident in Figure 3.20.A. This image also clearly shows the

replacement of quartz by a very fine-grained aggregated, colourless mineral. Microprobe analyses of this mineral show that it is an Al-Na zeolite, namely natrolite. These analyses are given in Table 3.9. Natrolite $[\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot\text{H}_2\text{O}]$ has been described, in several studies, as occurring in sedimentary rocks. These studies are outlined by Gottardi and Galli (1985). Sediments in Tanzania show natrolite as an alteration product of nepheline (Gottardi and Galli, 1985). As with most zeolites, however, natrolite is most commonly the product of hydrothermal activity relating to igneous processes and Gottardi and Galli (1985) provide a list of such occurrences. One such occurrence is in the central parts of the Kola Peninsula, in the Lovozero alkali massif where natrolite is extensively found (Vlasov *et al.*, 1966). Although Gottardi and Galli (1985) classify natrolite as a fibrous zeolite, Vlasov *et al.* (1966) point out that various crystal habits of the mineral exist in the Lovozero massif. These habits range from prismatic, to fibrous, to acicular and even to chalcedonic (Vlasov *et al.*, 1966). Vlasov *et al.* (1966) also describe a fine-grained granular habit for natrolite. This habit is how natrolite is generally found in parts of drill core SLT-015. It is also found as medium-grained, anhedral crystals in some vugs where it is the dominant phase. In this case it generally contains small sérandite inclusions.

Table 3.9: Average of 11 microprobe analyses of natrolite in drill core SLT-015.

Oxide wt %	n = 11	Std. dev.
SiO ₂	47.01	0.52
Al ₂ O ₃	26.20	0.15
FeO	0.03	0.04
MnO	0.09	0.18
CaO	0.02	0.01
Na ₂ O	16.05	0.21
K ₂ O	0.03	0.02
Total	89.42	0.81
Cations calculated on the basis of 10 O:		
Si	3.01	
Al	1.98	
Fe	0.00	
Mn	0.01	
Ca	0.07	
Na	1.99	
K	0.00	
Water not determined		

Many vugs display a distinct phase zonation, as in Figure 3.20.B, where sheaf-like aggregates of sérandite grow inward into a core of quartz. The outer zone consists of fine-grained, aggregated natrolite and albite. Barium phases are present in this unit, forming part of the somewhat complex mineralogy of these vugs. The principal barium phase is barite which occurs as euhedral, blocky to columnar grains as shown in the backscattered electron image shown in Figure 3.20.C. Very fine-grained braunite occurs in the matrix of this unit as displayed in Figure 3.20.C. Hematite also occurs in the matrix. Calcite occurs in some vugs but is not abundant. Another accessory phase in this unit is the manganese epidote piemontite which occurs as fine-grained, reddish brown aggregates at vug boundaries in contact with the opaque matrix. This texture is shown in Figure 3.20.D.

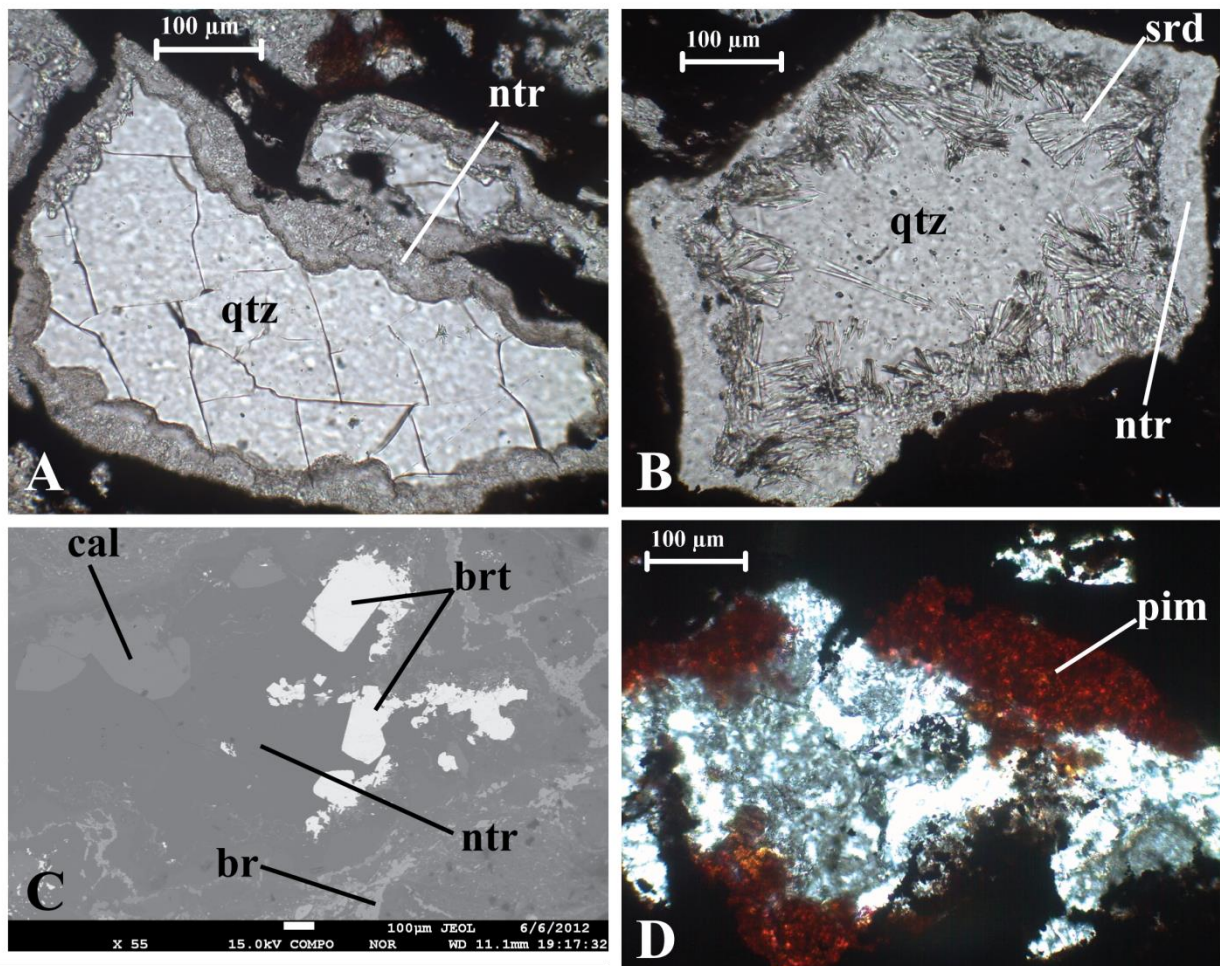


Figure 3.20: Various textures and mineral relationships as observed in the fine-grained breccia that occurs between the depths of 87 m and 88 m. All images are transmitted light photomicrographs unless otherwise stated. **A.** Fractured quartz grain replaced at the boundary by natrolite (PPL, sample 15-11Ci). **B.** Mineral zonation in a vug with a core of quartz, an inner zone of sheaf-like aggregates of sérandite and an outer zone of natrolite/albite. (PPL, sample 15-11B). **C.** Backscattered electron image of a barite-calcite-natrolite vug in a braunite-rich matrix (sample 15-11B). **D.** Fine aggregates of piemontite along a vug boundary, in contact with opaque matrix (XPL, sample 15-11Ci).

Piemontite, with the general formula $\text{Ca}_2(\text{Al,Mn}^{3+},\text{Fe}^{3+})_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$, typically occurs in rocks which are associated with low-grade metamorphism but it can also be produced by hydrothermal activity within manganese deposits (Deer *et al.*, 1992). Piemontite, as well as Sr-piemontite, is also found in the Kalahari Manganese Field (Gutzmer and Beukes, 1996b). Piemontite in this unit has low Fe content and high Mn and Al content as shown in Table 3.10. These elements seem to substitute freely for one another – this is also apparent in the mineral formula.

Table 3.10: Average of three microprobe spot analyses of fine-grained, aggregated piemontite in sample 15-11Cii.

Oxide Wt. %	n = 3	Std. Dev.
SiO ₂	38.57	0.28
CaO	21.52	0.27
K ₂ O	0.05	0.02
MgO	0.02	0.02
Al ₂ O ₃	22.03	0.42
Fe ₂ O ₃	1.17	0.08
Mn ₂ O ₃	15.02	0.44
TiO ₂	0.06	0.01
Na ₂ O	0.23	0.09
H ₂ O*	1.89	0.01
Total	100.56	0.34
Calculated on the basis of 12.5 O		
Si	3.05	
Ca	1.82	
K	0.01	
Mg	0	
Al	2.05	
Fe	0.07	
Mn	0.9	
Ti	0	
Na	0.03	
*Calculated according to piemontite mineral formula		

Other phases that are present in the microbreccia unit include minor pectolite as well as minor barytocalcite. These accessory phases occur only within vugs – the barytocalcite does not have any particular textural relationships; the pectolite, however, tends to occur as fine, blocky aggregates or laths that appear to grow from the vug boundaries toward the centre. The pectolite in this study is easily distinguishable from sérandite in thin section as it is brown in plane-polarized light. This unit contains each of the most barium-rich species in drill core SLT-015 and these are highlighted in

Table 3.11. Witherite and barite occur in more than one unit in drill core SLT-015 but barytocalcite has only been found in the microbreccia unit.

Table 3.11: Electron microprobe analyses of the three most Ba-rich species in drill core SLT-015.

Oxide wt. %	Witherite			Barytocalcite	Barite		
	n = 10	Std. Dev.	Range		n = 7	Std. Dev.	Range
MgO	0.01	0.02	<0.007 - 0.05	0.05	0.01	0.01	<0.007 - 0.02
FeO	0.01	0.02	<0.013 - 0.05	0.06	0.04	0.07	0.02 - 0.17
MnO	0.01	0.02	0.01 - 0.04	n.d	n.d	-	-
BaO	75.90	0.83	75.00 - 77.54	50.26	65.39	0.38	64.82 - 65.84
CaO	0.01	0.01	<0.003 - 0.02	19.66	0.03	0.03	<0.011 - 0.07
SrO	0.73	0.20	0.41 - 1.05	0.10	0.01	0.01	<0.01 - 0.03
SO ₃	n.d	-	-	0.02	34.1	0.23	33.80 - 34.44
CO ₂ *	22.66	0.45	22.00 - 23.30	30.00	n.d	-	-
Total	99.33	0.45	99.01 - 100.51	100.15	99.58	0.18	99.27 - 99.88

Cations calculated according to 1 CO₃ for witherite and barytocalcite and 4 O for barite

Mg	0.00	0.00	0.00
Fe	0.00	0.00	0.00
Mn	0.00	0.00	0.00
Ba	0.99	0.48	1.00
Ca	0.00	0.51	0.00
Sr	0.01	0.00	0.00
S	0.00	0.00	1.00

Abbreviations: n.d - not determined; n = number of analyses; * calculated based on witherite and barytocalcite formula

3.2.9. Siliceous hematite lutite and laminated ferromanganese ore

Two units exist in the upper sampled portion of drill core SLT-015 as shown in Figure 3.21. The first unit consists of hematite lutite which seems, in hand-specimen, to bear a siliceous overprinting.

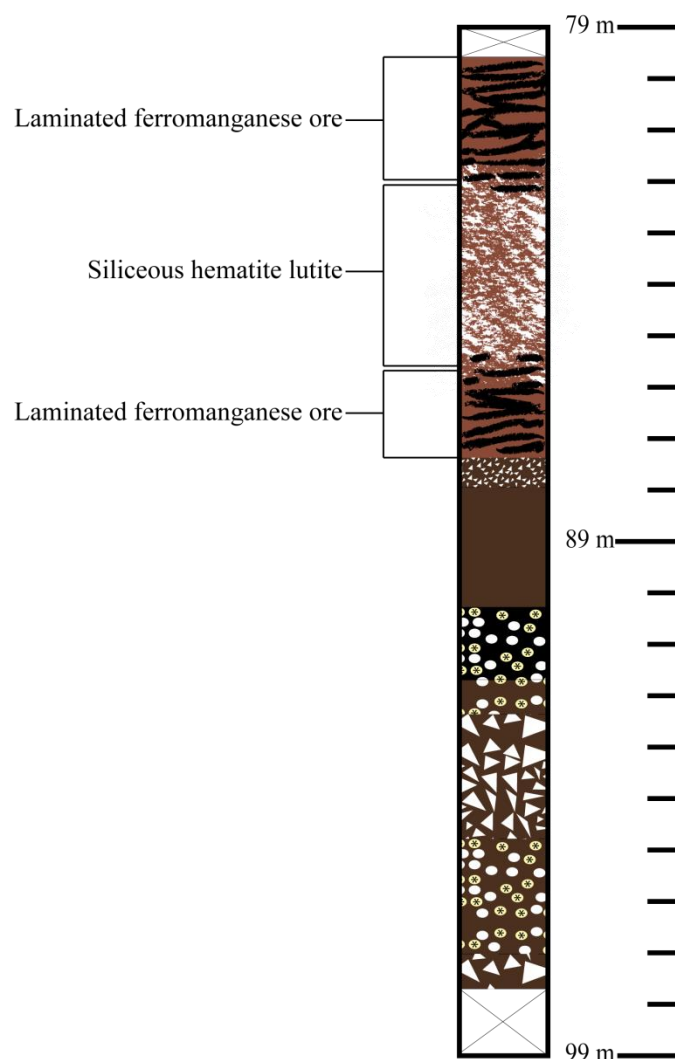


Figure 3.21: Stratigraphic positions of the siliceous hematite lutite unit and the laminated ferromanganese ore unit in drill core SLT-015.

Transmitted light microscopy (Figure 3.22.A) reveals that the silicate material consists of fine-grained ($<10\ \mu\text{m}$), aggregated mica. Bulk rock X-ray diffraction data, as represented by the graph given in Figure 3.22.C, confirms that the mica is paragonite. The peaks for paragonite are represented at the correct angle of 2θ ; however, the intensities of the respective peaks are not as they should be, based on various data from the literature. This is most likely due to preferred orientation of the paragonite grains during the packing of the powder for analysis. The XRD spectrum also shows that the two most abundant phases in this rock are hematite and paragonite with the hematite contributing the bulk of the opaque matrix. Paragonite is typically associated with greenschist-, amphibolite- and blueschist-facies metamorphic rocks, occurring as fine-grained aggregates (Deer *et al.*, 1992). However, it has also been found in fine-grained sedimentary rocks (Deer *et al.*, 1992).

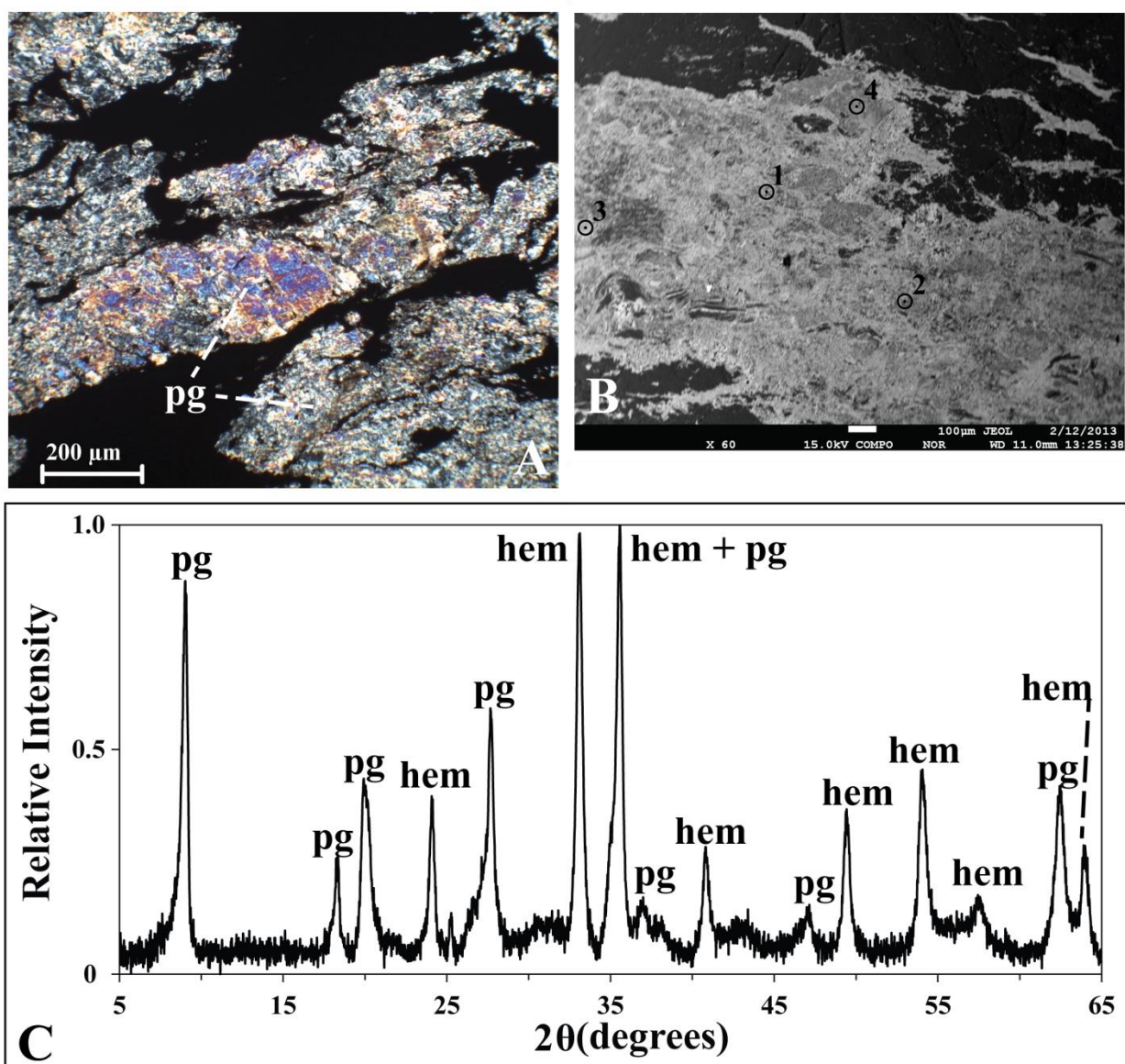


Figure 3.22: Petrography and mineralogy of the siliceous hematite lutite unit in the upper sampled portion of drill core SLT-015 as represented by sample 15-09. **A.** Transmitted light photomicrograph of fine-grained paragonite (XPL). **B.** Backscattered electron image showing the position of four analyses of opaque matrix performed using a 20 µm diameter beam. **C.** Bulk rock XRD spectrum of the siliceous hematite lutite showing the two dominant phases.

Microprobe analyses of the paragonite are presented as an average in Table 3.12. The Na and Al concentrations in paragonite from this drill core are lower than a typical paragonite (measured, in this case, by Zen *et al.* [1964]). This may be as a result of non-stoichiometry in the paragonite structure. Silicon substitution for Al can explain the lower concentration for the latter and the elevated concentration for the former. Thus the non-stoichiometric nature of the paragonite in SLT-015 can be attributed to vacancies in the sodium site. This also accounts for the lower total. Another

possibility may relate to the analytical process itself in that Na₂O was not being measured correctly with a lower diameter beam. It is perhaps possible that using a greater diameter beam may have improved the Na₂O values but this presents further problems in that multiple grains are analysed due to the very fine-grained nature of the paragonite. Whichever scenario is used, when both the microprobe analyses and the XRD spectrum are taken into account, little doubt remains that this mineral is paragonite. Table 3.12 also presents four microprobe analyses that were performed using a beam diameter of 20 µm which, although not at all accurate, provide a basic representation of what elements are present (and their relative abundance) in the opaque matrix in the hematite lutite unit. The four analyses represent mixed analyses of an extremely fine-grained matrix – the positions of the analyses are shown in Figure 3.22.B.

Table 3.12: Chemical compositions of paragonite in sample 15-09 (measured using a 10µm beam diameter) as well as that analysed by Zen *et al.* (1964). Also included are mixed analyses of the opaque matrix in 15-09 analysed with a 20 µm beam diameter.

Paragonite SLT-015			Paragonite	Opaque matrix			
Oxide Wt. %	n = 6	Std. Dev.	Zen <i>et al.</i> ., 1964	1	2	3	4
SiO ₂	48.76	0.43	47.00	22.16	17.46	11.69	11.72
CaO	0.03	0.01	0.24	0.03	0.08	0.03	0.05
K ₂ O	0.44	0.06	0.81	0.56	0.44	0.34	0.33
MgO	0.03	0.01	0.10	0.02	0.02	0.04	0.02
Al ₂ O ₃	37.54	0.18	39.10	19.99	15.84	10.46	10.27
Fe ₂ O ₃	-	-	0.78	48.31	55.27	63.41	26.62
FeO	0.56	0.40	-	-	-	-	-
MnO	0.06	0.02	0.02	2.00	2.40	3.54	4.46
TiO ₂	0.00	0.00	0.02	1.41	1.79	2.93	42.03
Na ₂ O	5.31	0.17	7.50	1.82	1.37	0.67	0.82
Cr ₂ O ₃	0.02	0.02	-	0.54	0.73	0.57	0.18
Total*	92.75	0.36	95.57	96.83	95.39	93.67	96.50
Cation ratios calculated on the basis of 11 O:							
Si	3.16		3.00				
Ca	0.00		0.02				
K	0.04		0.07				
Mg	0.00		0.01				
Al	2.86		2.94				
Fe	0.03		0.04				
Mn	0.00		0.00				
Ti	0.00		0.00				
Na	0.67		0.93				
Cr	0.00		-				

* Totals exclude hydrous fraction

Fe_2O_3 constitutes the highest concentrations within the matrix; this is due to an abundance of cryptoplaty hematite. The SiO_2 , Al_2O_3 and Na_2O concentrations in the matrix are likely representative of extremely fine-grained paragonite in the interstices between hematite grains. This is further supported by the positive correlation between Al_2O_3 and SiO_2 as illustrated in Figure 3.23 with the trend line intercepting very close to the origin. K_2O concentrations in all four matrix analyses do not exceed 0.6 wt. %.

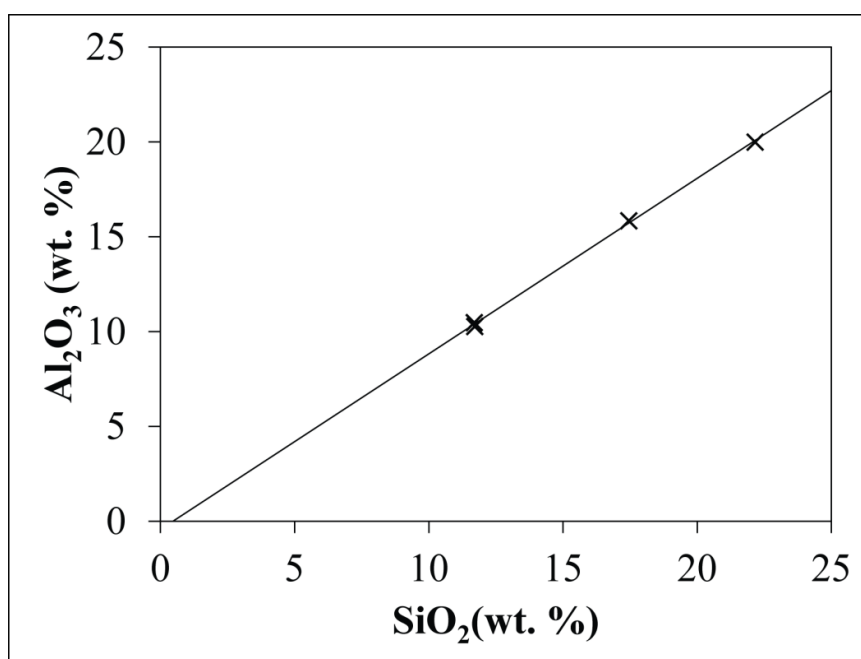


Figure 3.23: Graph of SiO_2 versus Al_2O_3 illustrating a positive correlation between the two oxides in the matrix of sample 15-09.

TiO_2 is present in all four of the matrix analyses presented in Table 3.12. However, analysis 4, in particular, contains ca. 42 wt. % TiO_2 which corresponds to a darker part of the opaque matrix in Figure 3.22.B. These darker patches, representing areas consisting of lighter elements than the surrounding Fe in the hematite, are perhaps extremely fine-grained alteration products of Ti-rich clasts which have pseudomorphed the original clast. The surrounding hematite-rich matrix contains around 1 wt. % TiO_2 . Finally, the MnO concentration in the four matrix analyses ranges between 2 wt. % and 5 wt. % with the highest concentration corresponding to the highest concentration of TiO_2 . The low totals in the opaque matrix analyses are attributed to two factors: firstly, the undetermined water content that would be present in any fine-grained paragonite present and secondly, the analyses included unavoidable, interstitial voids in the matrix.

The second unit in the upper portion of SLT-015 is described in Chapter 2 as laminated ferromanganese ore with intercalated lenses of brick-red hematite lutite. Reflected-light microscopy reveals similar features to those seen in hand specimen. The broad textural appearance of this unit is represented by Figure 3.24.A which shows massive, monomineralic, fine-grained crystalline braunite laminations alternating with extremely fine-grained, hematite-bearing clay or lutite. The clay matrix contains abundant, very fine-grained ($<10\ \mu\text{m}$) hematite which appears as the white phase in Figure 3.24.B – this explains the brick-red colour of the lutite. Some parts of the unit show alternating monomineralic laminations of fine-grained ($<50\ \mu\text{m}$) hematite and braunite as shown in Figure 3.24.C. Braunite is the dominant phase in this unit and occurs not only as described above but as very finely laminated crystalline braunite intercalated with extremely fine-grained clay (Figure 3.24.D).

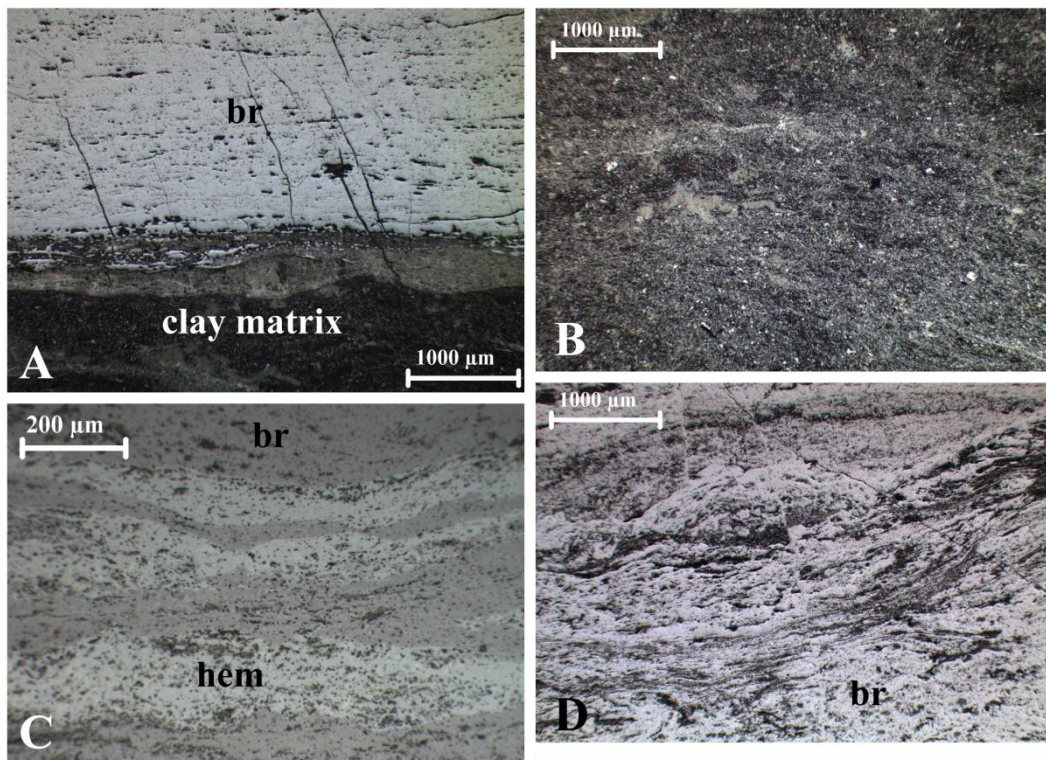


Figure 3.24: Reflected-light photomicrographs of the laminated ferromanganese ore in the upper sampled portion of drill core SLT-015. **A.** Fine-grained, crystalline braunite laminations alternating with extremely fine-grained, hematite-bearing lutite laminations (Sample 15-02). **B.** Typical massive lutite with abundant white, very fine-grained hematite (Sample 15-02). **C.** Alternating monomineralic hematite (light) and braunite (dark) laminations (Sample 15-01). **D.** Very fine laminations of fine-grained, crystalline braunite with intercalated lutite (Sample 15-01).

Discrete silicate phases cannot be observed under the microscope in this unit but bulk rock XRD analysis of the clay matrix from a representative sample reveals the presence of both hematite and paragonite (Figure 3.25). The paragonite is of submicroscopic size in this unit and thus is not observed in thin section – similar to the assumed paragonite from microprobe analyses of the opaque matrix in the siliceous hematite lutite unit.

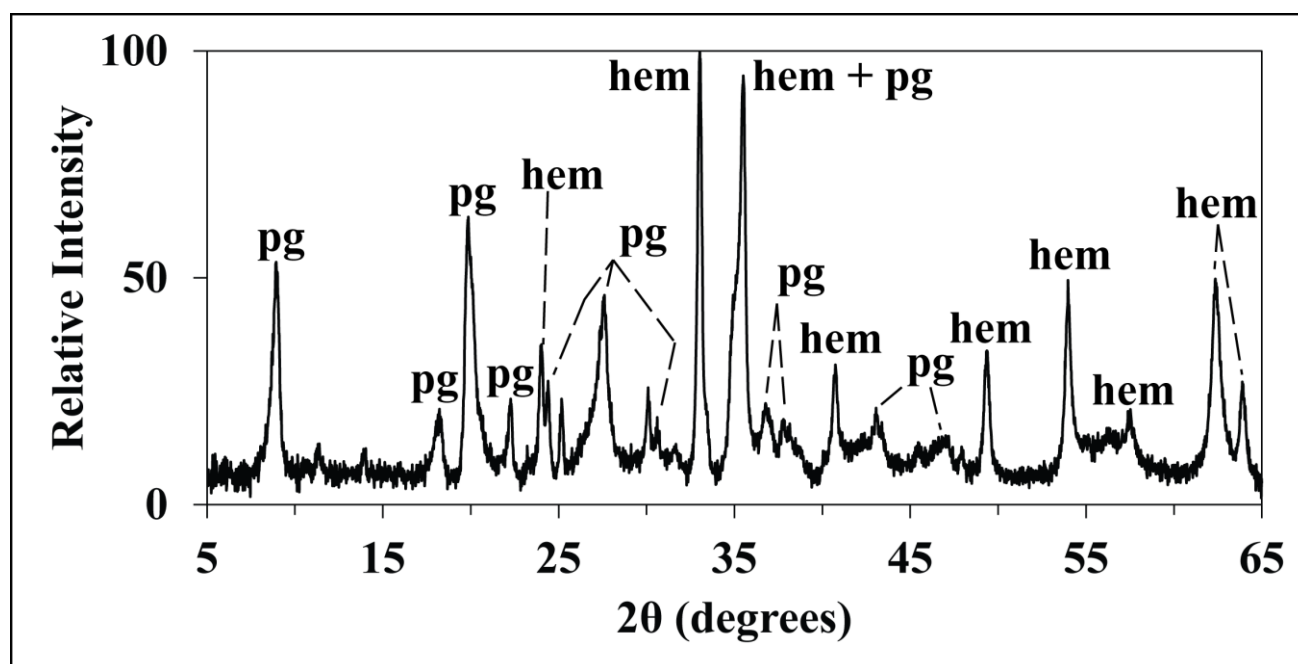


Figure 3.25: Bulk rock XRD spectrum of hematite lutite in the laminated ferromanganese ore unit in the upper sampled portion of drill core SLT-015 (Sample 15-02). Hematite is the dominant phase but strong peaks for paragonite are also present.

3.2.10. Summary

Drill core SLT-015 contains a wide variety of mineral species which vary across the orebody from the base toward the top. The lowermost unit is mineralogically simple with quartz and hematite being the two main phases. The quartz occurs as aggregates of chert and as colloform-textured chert. Coarse-grained, euhedral quartz is also prevalent. The mineralogical complexity of the orebody increases in shallower units. Sérandite, aegirine, albite and orthoclase and rare minerals such as arsenotokyoite and noélbensonite fill open spaces within a hematite-braunite-dominated matrix. Some replacement of authigenic coarse-grained quartz is also apparent. Witherite is also a major phase, particularly in the lower units containing a wide variety of gangue phases, where it occurs as

coarse, euhedral grains. Various replacement textures exist in these lower units – noélbensonite and arsenotokyoite, often occurring together, replace sérandite and witherite has also been seen to replace sérandite. Microcline occurs as adularia, mostly growing inward, toward the centre of vugs from the boundaries. Toward the centre of the orebody aegirine is less common, occurring as coarse, euhedral grains in small vugs. Albite is a common gangue phase in the central units and tends to occur at vug boundaries with calcite in the cores. Another zonal texture in this unit occurs where sérandite sheaves grow at vug boundaries with quartz forming a central core and natrolite forming the outermost zone. Sérandite is abundant in these units, partially or completely replacing quartz and sometimes pseudomorphously doing so. Braunite and hematite are the main ore minerals in the matrix. The hematite generally occurs as cryptoplaty grains whereas the braunite is crystalline. Toward the upper part of the orebody, two main units occur. One consists of hematite lutite which also contains fine, aggregated paragonite; the other consists of laminated clay, hematite and braunite. Very few gangue minerals exist in these upper units.

3.3. **Diamond Drill Core SLT-017**

Diamond drill core SLT-017 is affected by faulting thus the sampled portion of the core does not contain clasts that would otherwise reflect the basal part of the ferromanganese orebody. Therefore the sampled section of SLT-017 most likely represents the upper limits of the orebody – this is supported by the contact between the orebody and the overlying, ferruginised conglomerate (i.e. the Doornfontein Conglomerate) which is known to be the hanging wall of the ferruginous ores of the Western Belt (Gutzmer and Beukes, 1996a). Both the ferruginised conglomerate and the manganese ore were analysed petrographically. The following observations were made.

The ferromanganese ore shows consistency texturally and mineralogically throughout the body. It is, for the most part, very fine-grained (<20 µm) and generally consists of laminated ore and shale-like, ferruginised matrix. Braunite is the dominant ore phase and it occurs either as fine, crystalline laminations or as coarser crystalline masses. Hematite is also present, generally occurring as specularite (where grain sizes range from 50 to 100 µm). Figure 3.26 shows the typical texture found in the ferromanganese ore of drill core SLT-017. This figure illustrates the distribution of Fe, Mn, Si, Ba, Na and Al in a typical sample from the ferromanganese ore. The most striking of the element maps shown are the Ba, Al and Mn maps. The Mn map clearly outlines the distribution of

braunite-rich clasts as it is all found within this phase. No manganese is present in the shale matrix. This is in stark contrast to the Al distribution as this element is particularly concentrated in the matrix as to be expected in a shale-like matrix. Braunite does tend to contain some aluminium and this is reflected in the Al distribution map. Sodium is also present in the matrix in smaller concentrations. The matrix is also Si-rich as reflected in the Si distribution map in Figure 3.26. Silicon is obviously also present in braunite but in lower concentrations than exists in the matrix.

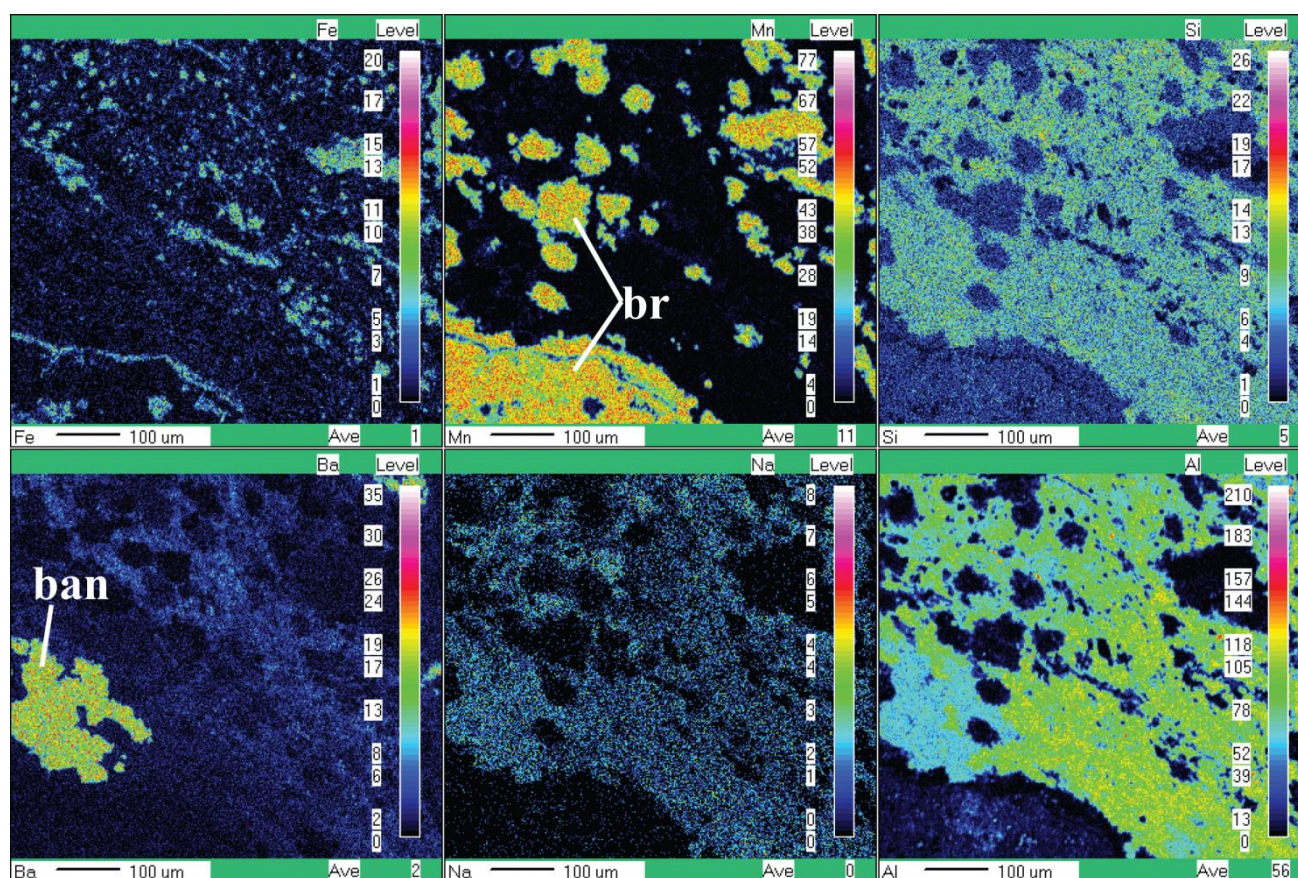


Figure 3.26: Relative concentrations of Fe, Mn, Si, Ba, Na and Al in electron microprobe element distribution maps from sample 17-18 in drill core SLT-017. Scales represent counts per second.

Barium is predominantly present in one phase in this drill core as shown in the Ba distribution map in Figure 3.26. This mineral is banalsite which is named for its composition: $\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$ (Campbell Smith *et al.*, 1944). It was first found in veins cross-cutting tephroite-rich manganese ore in Wales (Campbell Smith *et al.*, 1944). It is more commonly found in conjunction with its Sr end-member (stronalsite) in alkaline igneous rocks such as in the Pilansberg peralkaline complex in

South Africa (Liferovich *et al.*, 2006). Banalsite has also been described from metamorphosed bedded manganese ores in Japan (Matsubara, 1985).

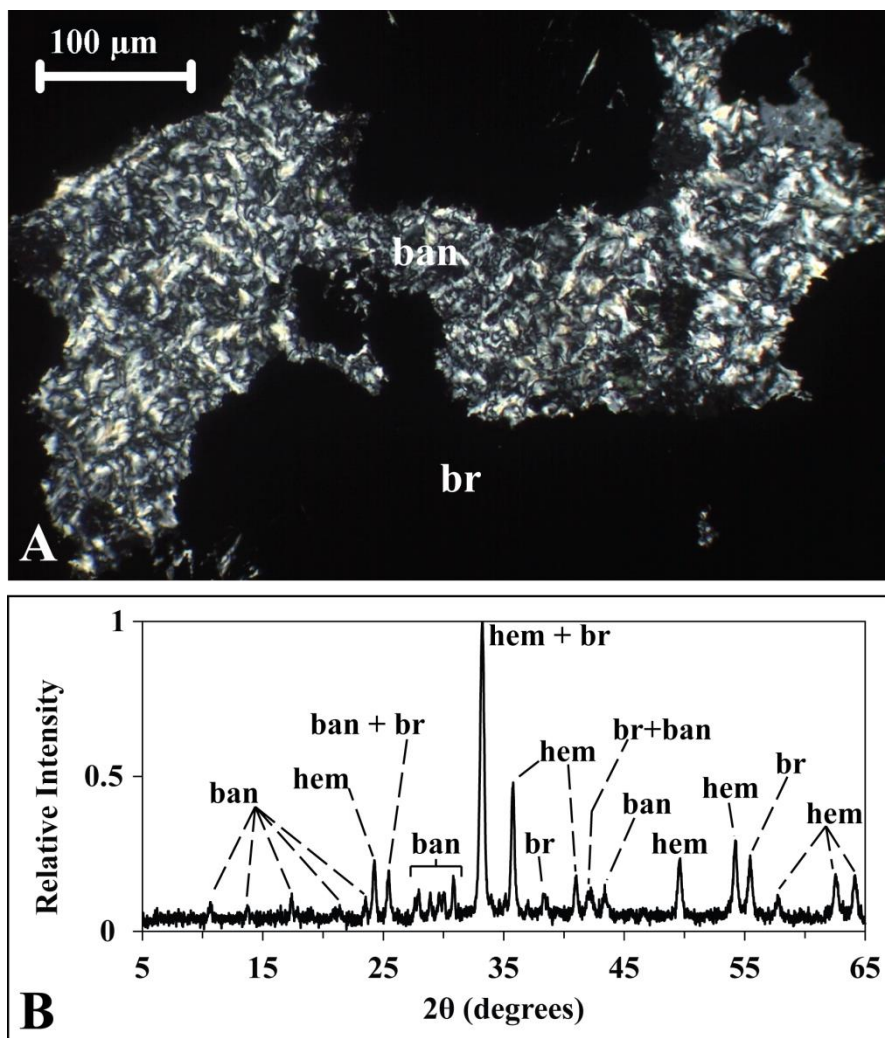


Figure 3.27: Banalsite, braunite and hematite in SLT-017. **A.** Transmitted light photomicrograph of vug-filling banalsite with an opaque matrix of braunite (XPL, sample 17-17). **B.** Bulk rock XRD spectrum showing hematite, braunite and banalsite in drill core SLT-017 (sample 17-16).

In the present study, banalsite develops as fine-grained aggregates in vugs and veinlets throughout the ore as shown in Figure 3.27.A. Bulk rock XRD analysis (Figure 3.27.B) of one sample from the ferromanganese ore of SLT-017 reveals a multiphase spectrum. The two dominant phases are hematite and braunite but banalsite is also present in such proportions as to also impact the spectrum. Other XRD analyses taken across the orebody reveal similar spectra with the main difference

between samples being the varying proportions of hematite to braunite. The fine-grained nature of the banalsite made analysis by microprobe difficult but one reasonably accurate analysis is shown in Table 3.13.

Table 3.13: Single microprobe analysis of banalsite from the sample 17-18.

Oxide wt. %	n = 1
SiO ₂	35.47
Al ₂ O ₃	31.12
BaO	21.36
FeO	0.42
MnO	0.74
K ₂ O	0.03
Na ₂ O	10.07
Total	99.21
Cations calculated on the basis of 16 O	
Si	3.91
Al	4.05
Ba	0.92
Fe	0.04
Mn	0.07
K	0.00
Na	2.15

Paragonite has also been identified in drill core SLT-017. Although this mineral was not identified in petrographic observations under the microscope, it has been identified as a minor constituent of some samples by XRD. This is shown in Figure 3.28. This bulk rock powder XRD spectrum also shows that this particular sample contains an abundance of hematite as well as some banalsite.

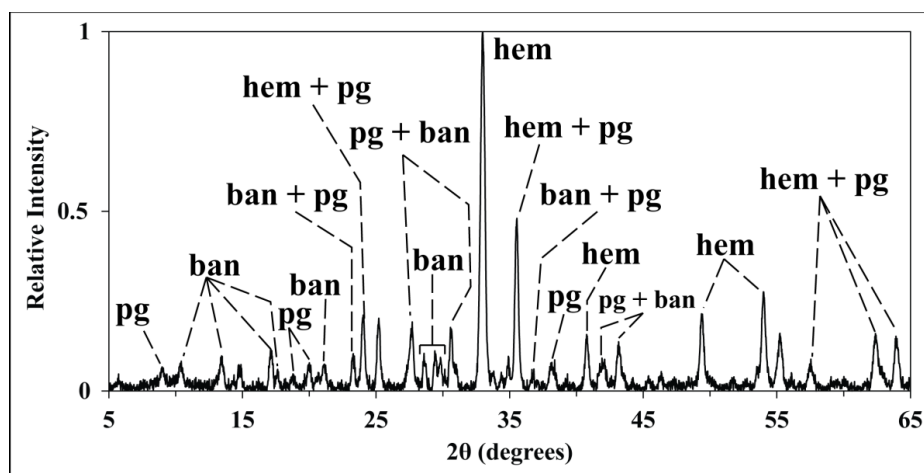


Figure 3.28: Bulk-rock XRD spectrum of sample 17-15 from the ferromanganese ore unit.

Poorly sorted, ferruginised conglomerate conformably overlies the ferromanganese ore. The basal portion of this unit consists of ferruginised banded iron formation clasts as well as some quartz clasts. Minor barite is also present. The matrix consists of ferruginised shale in some places but mostly it consists of fine-grained (<50 µm) hematite. Of particular interest in this basal portion is the replacement of quartz clasts by braunite as illustrated in Figure 3.29. Here braunite is partially replacing quartz clasts; however, in some places, braunite can be found completely replacing these clasts.

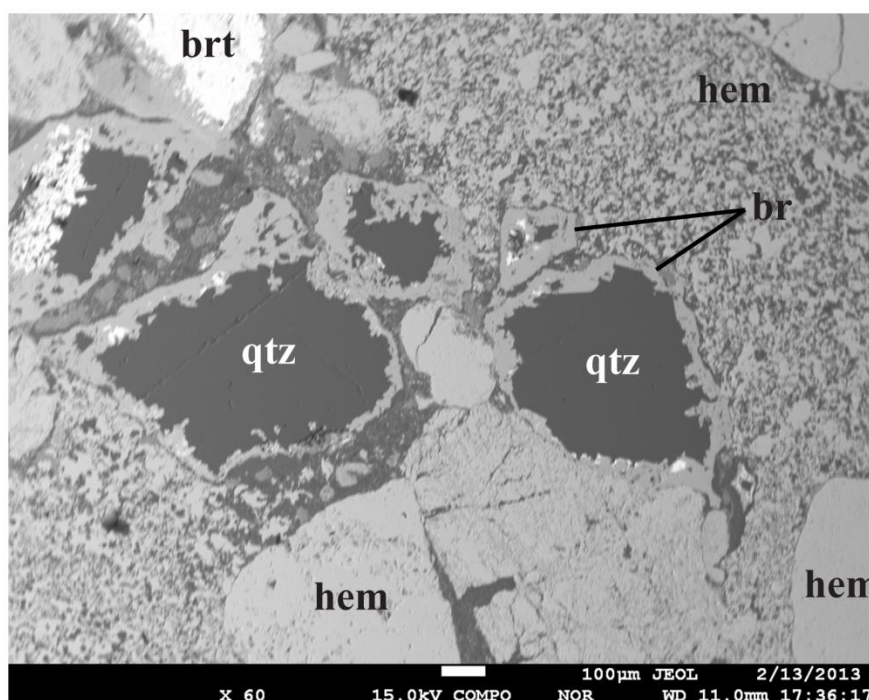


Figure 3.29: Backscattered electron image of braunite replacing quartz clasts in ferruginised conglomerate from drill core SLT-017 (sample 17-12).

Braunite does not occur further up in the conglomerate where hematite is by far the dominant mineral occurring both in coarse crystalline form (particularly in clasts) as well as very fine-grained (>20 µm) hematite in the matrix. Figure 3.30 provides some examples of typical textures found in the ferruginised conglomerate of drill core SLT-017. The conglomerate is very poorly sorted and many clasts show original laminations, presumably of banded iron-formation (Figure 3.30.A). The clasts also range from angular to rounded as shown in Figure 3.30.B. This figure also shows that shale clasts are also present in the conglomerate and further illustrates the poorly sorted nature of the clasts.

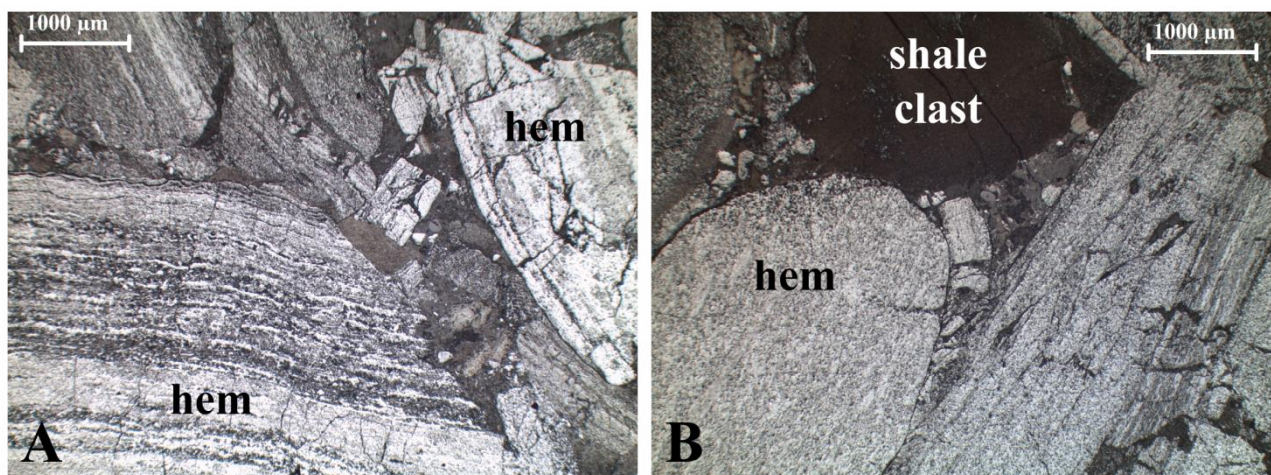


Figure 3.30: Reflected-light photomicrographs of textures in ferruginised conglomerate from drill core SLT-017. **A.** Angular clasts of ferruginised banded iron-formation with original laminations preserved (sample 17-09). **B.** Adjacent hematite-rich, angular and rounded clasts as well as shale clasts (sample 17-10).

3.4. Diamond Drill Core AKH-49

Moore *et al.* (2011) have discussed the petrography and mineral chemistry of this drill core. This thesis, therefore, aims to draw similarities between this drill core and SLT-015 and SLT-017 using new thin sections cut from various parts of AKH-49 as well as information sourced from Moore *et al.* (2011). Gangue phases described by Moore *et al.* (2011) and found as vug-fills in drill core AKH-49 are shown in Table 3.14. Common elements in most of the minerals in Table 3.14 are Na, K and Al as well as Mn. However, Li is also present in two of the gangue phases, namely norrishite and sugilite. The minerals listed in Table 3.14 are interpreted, by Moore *et al.* (2011), to have formed by the interaction of a Na-, K- and Li-rich fluid with the Mn-rich (and Al-bearing) host rocks.

The matrix to clast ratio in drill core AKH-49 is much greater than that in drill core SLT-015, especially toward the lower portion of the sampled sections. The lower parts of drill core AKH-49 predominantly consist of angular clasts of aggregated, coarse-grained quartz in alternating laminations of braunite- and hematite-bearing mudstone. The clasts also tend to show crude lamination or bedding. Hematite ooids are present in some parts of the matrix whereas some laminations consist almost entirely of fine-grained, crystalline braunite.

Table 3.14: Gangue phases present in drill core AKH-49 (after Moore *et al.*, 2011).

Mineral Name	Mineral Formula
Aegirine	$\text{NaFe}^{3+}\text{Si}_2\text{O}_6$
Albite	$\text{NaAlSi}_3\text{O}_8$
Armbrusterite	$\text{Na}_6\text{K}_5\text{Mn}^{3+}\text{Mn}^{2+}_{14}(\text{Si}_9\text{O}_{22})_4(\text{OH})_{10}\cdot 4\text{H}_2\text{O}$
Kentrolite	$\text{Pb}_2\text{Mn}^{3+}_2\text{O}_2(\text{Si}_2\text{O}_7)$
K-Feldspar (Microcline)	KAlSi_3O_8
Norrishite	$\text{KLiMn}^{3+}_2\text{Si}_4\text{O}_{12}$
Sérandite	$\text{NaMn}^{2+}_2\text{Si}_3\text{O}_8(\text{OH})$
Strontianite	SrCO_3
Sugilite	$\text{KNa}_2(\text{Fe}^{3+}, \text{Mn}^{3+}\text{Al})_2\text{Li}_3\text{Si}_{12}\text{O}_{30}$
Quartz	SiO_2
Witherite	BaCO_3

Where such massive braunite occurs, quartz-filled vugs are enveloped by subhedral to euhedral braunite grains as shown in Figure 3.31.A. In the shallower portions of the stratigraphy intersected by drill core AKH-49, as in SLT-015, the complexity of the mineralogy increases. Here coarse (up to $\sim 300\ \mu\text{m}$), euhedral albite fills large vugs (Figure 3.31.B). At even shallower depths in drill core AKH-49, irregular-shaped vugs are filled by minerals which show a general phase zonation as described by Moore *et al.* (2011). Figure 3.31.C shows aggregated sheaves of brown armbrusterite with an average grain size of approx. $50\ \mu\text{m}$ enveloping a central core of purple sugilite. Lesser sérandite and witherite also occur in the armbrusterite zone and fine-grained (20 to $100\ \mu\text{m}$) albite lines the boundaries of the vugs. Other vugs show abundant radiating aggregates of sérandite with large cores of witherite. These vugs also show a general zoning of albite as the outer zone, sérandite-pectolite as a middle zone and a witherite core. Armbrusterite is also present in these vugs in small modal amounts.

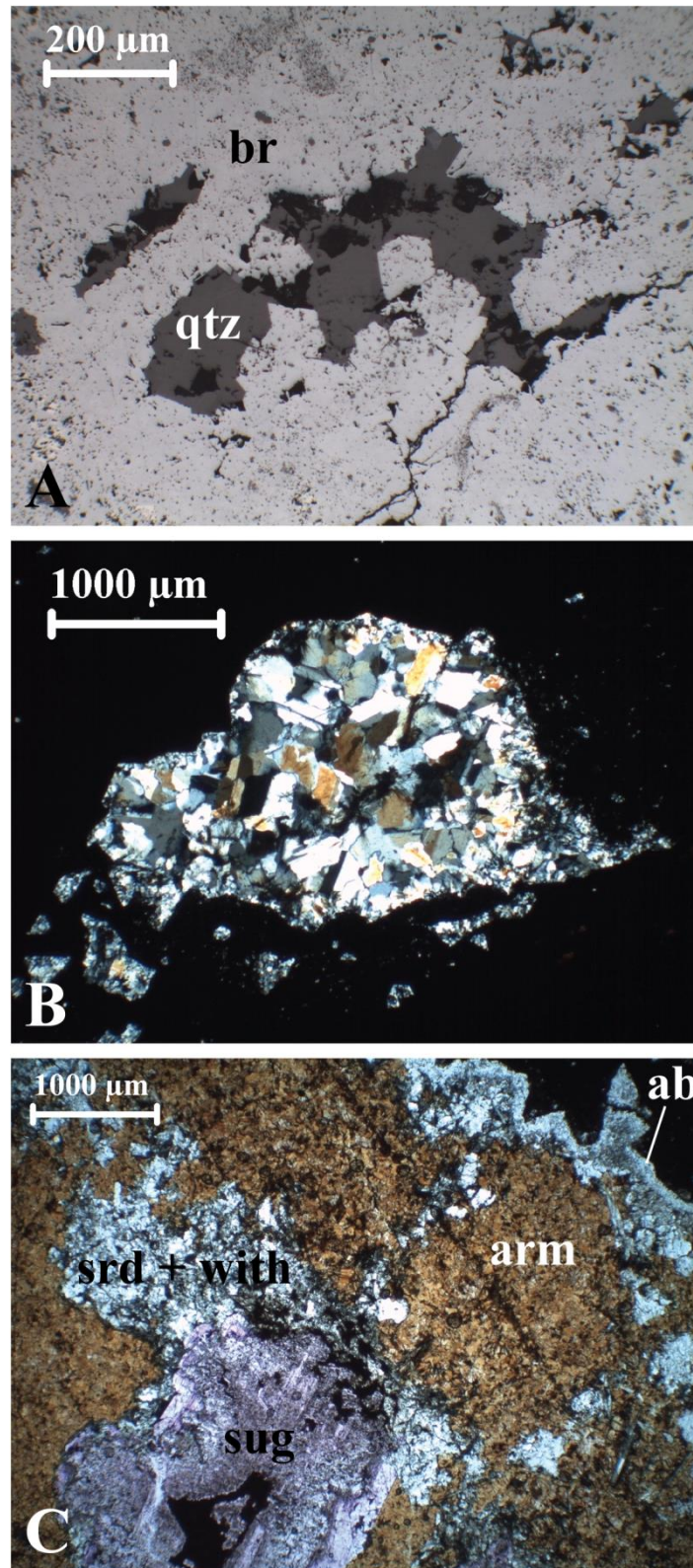


Figure 3.31: Photomicrographs of samples from drill core AKH-49. **A.** Subhedral to euhedral braunite grains surrounding a quartz-filled vug (Reflected light, sample AKH49-A). **B.** Albite-dominated vug (XPL, sample AKH49-E). **C.** Part of a large, irregular-shaped vug filled with armbrusterite, sugilite, albite and lesser sérandite and witherite in distinct zones (PPL, sample AKH49-D).

Some of the textures observed in AKH49 show marked similarities to textures observed in drill core SLT-015. Where braunite envelopes gangue clasts in AKH49, similar features are observed in the vuggy manganese ore unit in SLT-015. Albite-lined vugs are common to both drill cores. Zonal textures, although not widespread in SLT-015, are also observed in both drill cores. The phases that make up such zoned vugs are also similar with albite and sérandite showing similar textural features in both drill cores.

3.5. Diamond Drill Core SLT-018

This drill core captures Campbellrand dolomites in the deepest part of the core. This section briefly highlights some of the petrographic characteristics observed. Although a large proportion of the rock consists of dolomite, chert is also pervasive throughout. Figure 3.32.A shows chert adjacent to coarse-grained dolomite. In general the dolomite tends to be anhedral and varies in grain size from less than half a millimetre up to 3 mm. Figure 3.32.B shows a quartz vein crosscutting massive dolomite. Veins of specularite are present in some samples and apatite occurs as an accessory phase.

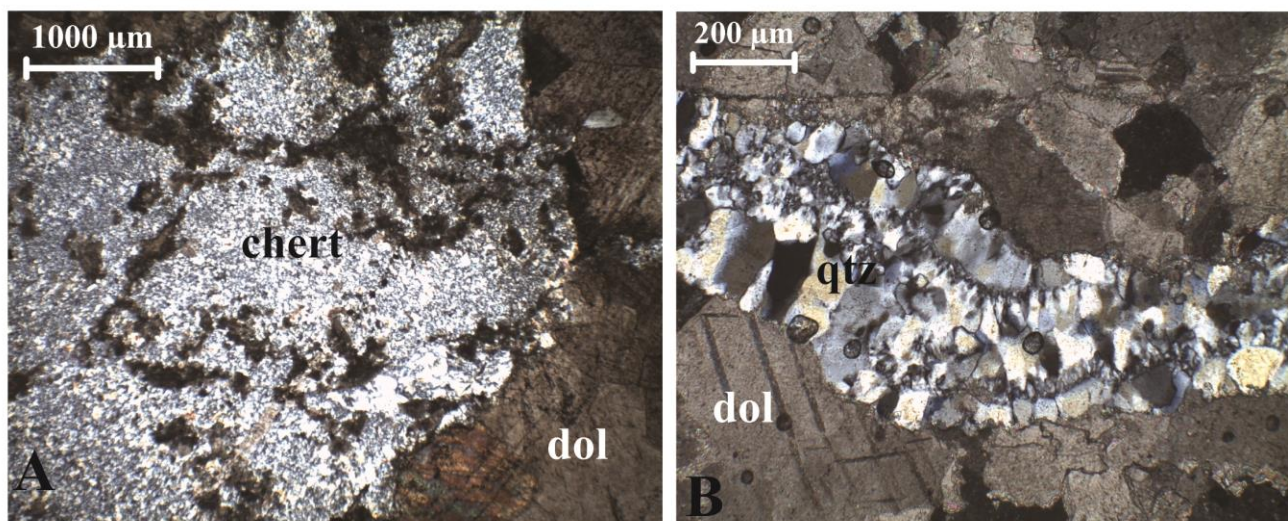


Figure 3.32: Photomicrographs of chert-bearing dolomites of the upper Campbellrand Subgroup. **A.** Chert adjacent to coarse-grained dolomite (XPL, sample 18-17). **B.** Quartz vein cross-cutting massive dolomite (XPL, sample 18-18).

One microprobe analysis of the dolomite reveals the presence of up to 4 wt. % Mn substituting into the mineral structure. This is shown in Table 3.15. Such Mn-rich dolomite serves as an excellent source of manganese for the development of manganese residual ore (Plehwe-Leisen and Klemm, 1995, Gutzmer and Beukes, 1996a).

Table 3.15: Single microprobe analysis of Mn-rich dolomite in drill core SLT-018.

Oxide wt. %	n = 1
CO ₂ *	46.50
FeO	2.66
MnO	4.37
MgO	17.78
CaO	29.04
BaO	0.02
SrO	0.01
SO ₃	0.02
Total	100.39
Cations calculated according to 1 O	
Fe	0.03
Mn	0.06
Mg	0.42
Ca	0.49
Ba	0.00
Sr	0.00
S	0.00
*CO ₂ calculated according to dolomite formula	

3.6. Summary

Drill core SLT-015 contains a complex gangue assemblage. However, the base of the orebody consists almost exclusively of quartz/chert clasts and a hematite matrix. Between the lower and upper clast-supported breccia units is a matrix-supported unit which contains microcline, witherite, sérandite, and such rare minerals as noélbensonite and arsenotokyoite (As-bearing tokyoite). Further up in the orebody aegirine and albite also become important. These minerals occur with other accessory phases such as barite, strontianite, piemontite, barytocalcite, calcite and natrolite.

Paragonite is also an important mineral that occurs toward the top of the orebody. Various replacement textures are observed in this drill core. Such replacements include pseudomorphous replacement of quartz by sérandite, pseudomorphous replacement of sérandite by witherite, noélbensonite and arsenotokyoite, replacement of gangue by braunite and replacement of quartz by natrolite. Ore minerals in this drill core include braunite, partridgeite and hematite. Hollandite is also found but only in one unit.

Drill core SLT-017 is dominated by hematite and braunite but the mineral banalsite is also present in veinlets and vugs. This mineral is very fine-grained and occurs throughout the orebody. Paragonite has also been identified in this drill core. The contact between the ferromanganese ore unit and the overlying ferruginised conglomerate is sharp. Immediately above this contact gangue clasts (mainly quartz) are partially (sometimes completely) replaced by braunite. Some barite is also present. Hematite dominates the conglomerate and clasts consist of hematitized BIF clasts. Some of these clasts still show original laminations.

The AKH-49 drill core also contains a complex assemblage of minerals such as sugilite, armbrusterite, microcline, albite, sérandite-pectolite, witherite and aegirine (this study; Moore *et al.*, 2011). Moore *et al.* (2011) also identified kentrolite and a norrishite-like mineral. These minerals occur in vugs and some of the vug-filling assemblages are mineralogically zoned. This is similar to zoning in vugs of SLT-015. Quartz/chert is abundant in the matrix and in vugs of drill core AKH-49. Braunite and hematite form the ore minerals of this drill core. Finally, SLT-018 samples the Campbellrand dolomite immediately below the Wolhaarkop breccia. Here veins of coarse-grained quartz occur. Chert is also abundant and chalcedony is also present. The dolomite grain-sizes vary greatly from fine-grained (<50 µm) to coarse-grained (>1000 µm). These dolomites contain up to 4 wt. % MnO and serve as a good source of the metal for manganese ore formation as suggested by Plehwe-Leisen and Klemm (1995) and Gutzmer and Beukes (1996a). The variety of minerals found in all the studied drill cores is summarized in Table 3.16.

Table 3.16: Summary of minerals present in the four drill cores of this study and that found in AKH-49 by Moore *et al.* (2011).

Name	Formula	AKH-49	SLT-015	SLT-017	SLT-018
Aegirine	$\text{NaFe}^{3+}\text{Si}_2\text{O}_6$	X	X		
Aegirine-augite			X		
Albite	$\text{NaAlSi}_3\text{O}_8$	X	X		
Apatite					X
Armbrusterite	$\text{Na}_6\text{K}_5\text{Mn}^{3+}\text{Mn}^{2+}_{14}[\text{Si}_9\text{O}_{22}]_4(\text{OH})_{10}\cdot 4\text{H}_2\text{O}$	X			
Banalsite	$\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$			X	
Barite	BaSO_4		X		
Barytocalcite	$\text{BaCa}(\text{CO}_3)_2$		X		
Braunite	$\text{Mn}^{2+}\text{Mn}^{3+}_6\text{O}_8\text{SiO}_4$	X	X	X	
Calcite	CaCO_3		X		
Dolomite	$\text{CaMg}(\text{CO}_3)_2$				X
Hematite	Fe_2O_3	X	X	X	X
Hollandite	$\text{Ba}(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$		X		
K-feldspar	KAlSi_3O_8	X	X		
Kentrolite	$\text{Pb}_2\text{Mn}^{3+}_2\text{O}_2(\text{Si}_2\text{O}_7)$	X			
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot\text{H}_2\text{O}$		X		
Noelbensonite	$\text{BaMn}^{3+}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$		X		
Norrishite	$\text{KLiMn}^{3+}_2\text{Si}_4\text{O}_{12}$	X			
Paragonite	$\text{NaAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$		X	X	
Partridgeite	Mn_2O_3		X		
Pectolite	$\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$	X	X		
Piemontite	$\text{Ca}_2(\text{Al}, \text{Mn}^{3+}, \text{Fe}^{3+})_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$		X		
Quartz/Chert	SiO_2	X	X		X
Serandite	$\text{NaMn}^{2+}_2\text{Si}_3\text{O}_8(\text{OH})$	X	X		
Sericite		X			
Strontianite	SrCO_3	X	X		
Sugilite	$\text{KNa}_2(\text{Fe}^{3+}, \text{Mn}^{3+}, \text{Al})_2\text{Li}_3\text{Si}_{12}\text{O}_{30}$	X			
Arsenotokyoite	$\text{Ba}_2\text{Mn}^{3+}[(\text{As}, \text{V})\text{O}_4]_2(\text{OH})$		X		
Witherite	BaCO_3	X	X		

Chapter 4

Bulk-Rock Geochemistry

Three of the four drill cores were sampled for bulk-rock geochemical analysis. Clasts and veins were avoided as much as possible so that samples consisted of homogenous matrix material. As the main focus of the thesis is on drill core SLT-015, the highest sample resolution is from this core. Within the SLT-015 drill core, the matrix was differentiated into two types based on appearance in hand specimen: red to light brown shale matrix and black ferromanganiferous matrix. Such a differentiation was not necessary for the AKH-49 and SLT-017. Bulk-rock compositions are useful for this suite of samples given their fine-grained nature. Moore *et al.* (2011) did not perform bulk rock geochemical analyses on drill core AKH-49 therefore this thesis aims to complement petrographic observations from that paper with bulk-rock geochemistry. Gutzmer (1996) carried out bulk rock analyses on both siliceous and ferruginous ores from the PMF. However, Gutzmer (1996) sampled at or very near surface (in defunct open cast mine pits) where rocks may have been affected by modern surficial processes such as weathering (although care was taken by the same author to avoid weathering crusts). Plehwe-Leisen and Klemm (1995), another of the more recent authors to suggest a model for ore formation in the PMF, did not perform any whole-rock analyses on the ores in question. The manganese ore bodies in drill cores SLT-015 and SLT-017 have hanging walls at depths of ca. 80 m and ca. 90 m respectively and are thus less likely to have been affected by modern weathering processes. The following sections thus describe the bulk rock major and trace element concentrations for drill cores SLT-015, SLT-017 and AKH-49. In this chapter, care must be taken, when observing apparent trends, to the statistical reliability of data from small data sets.

X-Ray Fluorescence (XRF) was used to determine bulk-rock major and trace element composition and these analyses were undertaken using the Philips PW1480 XRF at the Department of Geology, Rhodes University. Unusually high BaO was measured by back-calculation from powder pellets composed of measured dilutions of the original samples with SpecPure© silicon oxide. Appendix II provides further details pertaining to the methods used to produce the data presented in this chapter. For calibration and detection limit data the reader is referred to Appendix VI.

4.1. General

4.1.1. Drill core SLT-015

Two broad matrix types were identified in drill core SLT-015: shale matrix and ferromanganiferous matrix. This section will first describe the bulk-rock major and trace element geochemistry of the shale matrix and then of the ferromanganiferous matrix. The stratigraphic positions of the samples analysed for bulk-rock geochemistry are indicated in Figure 4.1.

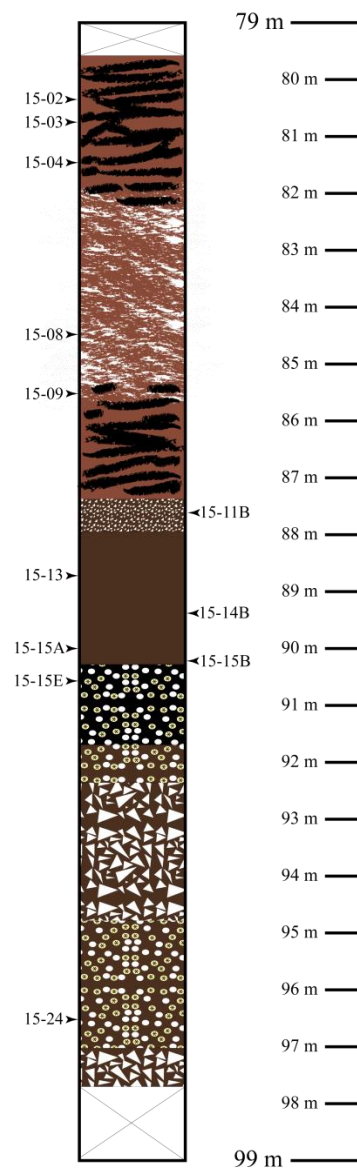


Figure 4.1: Stratigraphic position of samples analysed for bulk-rock geochemical data in SLT-015.

Table 4.1 provides bulk-rock major and trace element concentrations for the shale matrix. The dominant oxides in the shale matrix are SiO_2 , Al_2O_3 , Fe_2O_3 and Na_2O . The SiO_2 concentrations in the shale matrix range from 29.12 – 41.97 wt. %. This rock has Al_2O_3 concentrations that range between 25 and 35 wt. %. Fe_2O_3 concentrations (7.62 – 32.76 wt. %) are also elevated in this matrix type, especially in relation to the MnO range (0.25 – 5.4 wt. %). The range of Na_2O concentrations (2.86 – 4.24 wt. %) is greater than that of K_2O (1.41 – 3.42 wt. %). TiO_2 concentrations are fairly consistent with a range of approximately 0.5 – 1.5 wt. %. MgO , CaO , and P_2O_5 have concentrations under 1 wt. %. Barium is reported in SLT-015 as BaO due to its large abundance in these rocks. BaO concentrations in the shale matrix range from 0.11 – 1.13 wt. %.

The highest trace element concentrations in the shale matrix belong to chromium which has a large range of 60 – 1373 ppm. Zinc, cobalt, thorium and niobium concentrations do not exceed 50 ppm and Cu concentrations do not exceed 150 ppm. Analyses for Mo and U are essentially all below detection limit. Nickel concentrations, however, are high with a range of 86 – 644 ppm. Vanadium has a large variation in concentrations in the shale matrix with a range of 23 – 378 ppm. Yttrium concentrations range from 12 to 96 ppm and rubidium concentrations range between 49 and 57 ppm. Zirconium, most likely from accessory, detrital zircons, has concentrations ranging between 130 and 571 ppm. Lead has concentrations between 35 and 121 ppm. Strontium has elevated values in relation to most of the other trace element concentrations with a range between 71 and 501 ppm.

Table 4.1: Bulk rock major and trace element concentrations from shale matrix in drill core SLT-015

Sample Number	SLT-015: Shale Matrix				
	15-02	15-08	15-09	15-11B	15-15E
Depth (m)	80.35	84.48	85.52	87.48	90.53
major elements (wt. %)					
SiO ₂	36.16	29.12	33.14	36.51	41.97
TiO ₂	1.18	1.27	1.33	1.35	0.71
Al ₂ O ₃	34.04	25.16	27.53	27.40	32.84
Fe ₂ O ₃	12.32	32.76	25.52	17.50	7.62
MnO	1.03	1.14	1.16	5.40	0.25
MgO	0.29	0.16	0.17	0.30	0.56
CaO	0.47	0.18	0.15	0.25	0.65
Na ₂ O	4.24	2.86	3.76	3.98	3.43
K ₂ O	1.41	1.60	1.60	2.06	3.42
P ₂ O ₅	0.15	0.05	0.04	0.13	0.43
BaO	1.13	0.23	0.15	0.11	0.33
LOI	5.77	4.41	4.72	4.71	5.56
H ₂ O ⁻	0.94	0.73	0.53	0.50	0.26
Total	99.13	99.66	99.77	100.20	98.01
trace elements (ppm)					
Zn	50	26	23	31	10
Cu	68	71	61	142	18
Ni	123	147	86	273	644
Co	47	45	32	19	11
Cr	160	1373	1068	108	60
V	34	378	253	111	23
Sc	40	58	66	21	8
Th	33	10	7	32	17
Pb	35	76	78	45	121
Rb	56	49	51	63	97
Mo	<1	2	<1	<1	<1
Nb	22	8	8	26	13
Zr	233	142	140	571	130
Y	40	12	16	59	96
U	<2	<3	<2	<2	<2
Sr	501	156	101	71	119

Key: n.d: not determined; ppm: parts per million;
wt. %: weight percent.

Table 4.2 shows the bulk rock major and trace element concentrations for ferromanganiferous samples in drill core SLT-015. MnO (2.98 – 60.4 wt. %) and Fe₂O₃ (19.8 – 75.49 wt. %) make up the highest concentrations in the ferromanganiferous shales. SiO₂ (2.16 – 10.82 wt. %) and Al₂O₃ (0.97 – 4.95 wt. %) make up the second most abundant oxides in these samples. The range of CaO in the ferromanganiferous matrix is 0.35 – 2.31 wt. %. The concentrations of TiO₂, MgO, Na₂O, P₂O₅ are all under 0.5 wt. % but the concentration of K₂O in these samples reaches a maximum of 1.72 wt. %. BaO concentrations are unusually high in this suite of samples, with a range of 0.38 – 2.66 wt. %.

Table 4.2: Bulk rock major and trace element concentrations from ferromanganiferous matrix in drill core SLT-015.

Sample	SLT-015: Ferromanganiferous Matrix						
Number	15-03	15-04	15-13	15-14B	15-15A	15-15B	15-24
Depth (m)	80.75	81.46	88.72	89.38	90	90.16	96.52
major elements (wt. %)							
SiO ₂	7.51	5.60	5.07	2.16	3.20	3.62	10.82
TiO ₂	0.16	0.46	0.16	0.10	0.06	0.11	0.24
Al ₂ O ₃	4.95	2.64	3.18	1.13	0.97	1.28	3.90
Fe ₂ O ₃	19.80	27.79	36.99	68.21	61.56	55.89	75.49
MnO	60.40	56.99	43.91	24.32	31.03	34.02	2.98
MgO	0.08	0.04	0.25	0.09	0.08	0.10	0.41
CaO	2.31	1.65	0.63	0.35	0.59	0.42	0.22
Na ₂ O	0.14	0.04	0.37	0.14	0.08	0.29	0.30
K ₂ O	0.03	0.23	1.72	0.10	0.03	0.03	1.39
P ₂ O ₅	0.20	0.25	0.18	0.13	0.14	0.04	0.13
BaO	2.66	2.32	2.60	0.70	0.51	0.46	0.38
LOI	1.95	1.59	4.12	1.37	0.92	1.04	1.32
H ₂ O ⁺	0.24	0.18	0.31	0.22	0.24	0.33	0.25
Total	100.43	99.76	99.48	99.02	99.41	97.64	97.81
trace elements (ppm)							
Zn	153	147	100	71	66	78	66
Cu	1504	1832	271	137	235	212	62
Ni	198	236	153	229	213	186	431
Co	54	55	13	23	16	16	54
Cr	109	216	141	127	101	109	128
V	160	253	137	121	144	130	86
Sc	51	117	11	2	6	6	8
Th	<6	9	14	<6	<6	8	<6
Pb	251	549	1003	503	387	410	179
Rb	<2	<3	33	4	<3	<3	63
Mo	<2	<2	<2	<3	3	<3	3
Nb	3	3	<2	<2	<2	<2	4
Zr	46	61	34	11	16	14	43
Y	19	21	24	46	30	27	56
U	<4	<5	<5	<5	<5	<5	<5
Sr	488	381	2165	521	377	474	204

Key: n.d: not determined; ppm: parts per million; wt. %: weight percent.

Trace element concentrations show substantial enrichment in some elements, although the ranges of these concentrations tend to be large. Copper is one such element where the range of concentrations is 62 – 1832 ppm. Lead and strontium also show large ranges with concentrations of 179 – 1003 ppm and 204 – 2165 ppm respectively. Zinc concentrations range from 71 – 153 ppm and nickel concentrations range from 186 – 431 ppm. Vanadium and chromium concentrations are similar with V concentrations ranging from 86 – 253 ppm and Cr concentrations ranging from 101 – 216 ppm. Cobalt, thorium, zirconium, rubidium and yttrium concentrations do not exceed 65 ppm. Scandium

ranges from 2 to 117 ppm in the ferromanganiferous matrix. Molybdenum, uranium and niobium concentrations are at or near detection limit.

4.1.2. Drill core SLT-017

Table 4.3 provides major and trace element concentrations for ferromanganese ore samples in drill core SLT-017. Fe₂O₃ (21.76 – 40.62 wt. %) and MnO (18.43 – 50.4 wt. %) concentrations make up the largest proportions of these samples.

Table 4.3: Bulk rock major and trace element concentrations of ferromanganiferous ore in drill core SLT-017.

Sample	SLT-017					
Number	17-14	17-15	17-16	17-17	17-18	17-19
Depth (m)	91.51	92.09	92.62	92.9	93.44	93.83
major elements (wt. %)						
SiO ₂	7.31	18.38	10.43	7.63	15.41	10.18
TiO ₂	0.10	0.73	0.49	0.21	0.63	0.13
Al ₂ O ₃	3.23	16.85	7.99	3.51	12.94	7.04
Fe ₂ O ₃	30.48	28.94	40.62	24.47	21.76	20.76
MnO	50.40	18.43	26.82	57.02	35.41	49.36
MgO	0.08	0.43	0.26	0.13	0.46	0.17
CaO	1.58	0.62	0.76	1.20	0.81	3.16
Na ₂ O	0.39	3.20	1.12	0.40	2.00	1.07
K ₂ O	0.11	0.27	0.17	0.16	0.44	0.10
P ₂ O ₅	0.87	0.03	0.19	0.46	0.09	0.39
BaO	2.48	5.98	6.93	1.14	5.12	3.10
LOI	0.80	2.81	1.08	1.43	2.40	2.64
H ₂ O ⁺	0.22	0.67	0.22	0.27	0.45	0.24
Total	98.07	97.34	97.08	98.03	97.91	98.34
trace elements (ppm)						
Zn	62	48	46	82	61	65
Cu	311	99	96	394	177	95
Ni	20	97	59	29	105	25
Co	16	26	28	21	28	7
Cr	113	131	153	123	124	118
V	174	<5	<6	242	27	78
Sc	12	26	19	18	29	8
Th	15	64	43	23	47	19
Pb	968	2677	2661	1441	2255	1202
Rb	3	10	6	5	16	2
Mo	<2	<2	<2	2	<2	<2
Nb	2	16	11	5	12	2
Zr	21	344	83	58	245	23
Y	18	49	18	36	30	9
U	<4	<3	<4	<4	5	<3
Sr	1463	1313	1184	361	947	1700

Key: n.d: not determined; ppm: parts per million;
wt. %: weight percent.

SiO₂ (7.31 – 18.38 wt. %) and Al₂O₃ (3.23 – 16.85 wt. %) form the second largest proportions in the ore. BaO is very abundant in these samples with concentrations ranging from 1.14 to 6.93 wt. %. Na₂O concentrations are within the range 0.39 – 3.2 wt. % and CaO concentrations range from 0.62 – 3.16 wt. %. TiO₂ and P₂O₅ concentrations do not exceed 1 wt. %. MgO and K₂O concentrations are even lower, not exceeding 0.5 wt. %.

Lead (968 – 2677 ppm) and strontium (361 – 1700) concentrations are highly enriched in this drill core relative to the ferromanganiferous matrix in SLT-015. Zinc and nickel concentrations do not exceed 105 ppm but copper concentrations range between 95 and 395 ppm. Cobalt concentrations are low with a range of 6 – 28 ppm. Chromium concentrations have a small range of 113 – 153 ppm. Vanadium is below detection for two samples; the remaining samples have a range of 27 – 242 ppm. Scandium, thorium, rubidium and yttrium concentrations do not exceed 65 ppm. Zirconium has a large range of 21 – 344 ppm. Molybdenum, niobium and uranium concentrations are either very close to or below the detection limit.

4.1.3. *Drill core AKH-49*

The major and trace element concentrations of samples from drill core AKH-49 are presented in Table 4.4. SiO₂ is the most abundant oxide in these samples with a range of concentrations between 40 and 67 wt. %. Al₂O₃ and Fe₂O₃ concentrations are also high in these samples with ranges of 8.97 – 32.62 wt. % and 6.33 – 19.84 wt. % respectively. Most samples have MnO concentrations that do not exceed 4 wt. % with the exception of only one sample which has a concentration of 12.05 wt. %. The MgO concentrations for all but one sample are very similar at around 0.7 wt. % with the exception being at 1.09 wt. %. CaO concentrations do not exceed 0.51 wt. % and P₂O₅ concentrations are negligible. Na₂O and K₂O concentrations are high with concentrations of 0.62 – 4.63 wt. % and 0.7 – 5.27 wt. % respectively. The amount of BaO is very high in these samples with a minimum concentration of 0.44 wt. % and a maximum of 4.29 wt. %. The TiO₂ concentrations are very low with only one sample exceeding 1 wt. %.

Lead is the most abundant trace element in this suite of samples with a range of 156 – 1162 ppm. Zinc and copper concentrations do not exceed 75 ppm. Nickel concentrations are similarly low in most samples except for two samples which have concentrations of 1371 and 295 ppm. Cobalt concentrations range between 26 and 91 ppm.

Table 4.4: Bulk rock major and trace element concentrations of matrix samples in drill core AKH-49.

Sample Number	AKH-049					
	49-S	49-G	49-1	49-4	49-7	49-12
Depth (m)	192.4	193.7	194.9	195.2	195.6	198
major elements (wt. %)						
SiO ₂	40.76	52.14	49.49	59.82	59.75	66.30
TiO ₂	1.32	0.78	0.35	0.71	0.72	0.68
Al ₂ O ₃	32.62	16.30	8.97	14.41	13.51	12.36
Fe ₂ O ₃	6.33	12.05	19.84	10.45	11.01	10.26
MnO	2.17	3.51	12.05	1.54	1.34	0.94
MgO	0.77	0.73	1.09	0.73	0.76	0.73
CaO	0.10	0.13	0.51	0.11	0.25	0.11
Na ₂ O	1.26	3.26	4.63	0.69	1.17	0.62
K ₂ O	5.27	3.36	0.70	3.85	4.73	4.29
P ₂ O ₅	0.03	0.07	0.03	0.05	0.06	0.06
BaO	4.27	3.92	0.44	4.29	3.79	1.45
LOI	6.27	2.13	0.64	2.33	1.65	1.95
H ₂ O ⁻	0.67	0.44	0.26	0.38	0.47	0.41
Total	101.8	98.81	99	99.35	99.2	100.2
trace elements (ppm)						
Zn	2	3	74	44	2	2
Cu	7	10	53	28	9	7
Ni	11	17	1371	295	16	13
Co	26	55	91	50	62	59
Cr	277	63	82	48	51	55
V	28	<4	21	<4	<3	5
Sc	24	16	19	10	9	13
Th	24	28	15	23	27	21
Pb	156	991	590	885	1162	576
Rb	128	93	13	96	99	117
Mo	<1	<1	1	<1	<1	<1
Nb	23	15	7	14	16	15
Zr	257	275	100	284	280	258
Y	60	47	107	105	114	76
U	<2	<2	<3	<2	<2	<2
Sr	201	264	94	181	176	84

Key: n.d: not determined; ppm: parts per million;
wt. %: weight percent.

The range of chromium concentrations is 48 – 277 ppm. Vanadium is below detection for three samples and the concentrations for the other three do not exceed 28 ppm. Scandium and thorium concentrations also do not exceed 28 ppm. Rubidium concentrations range from 13 to 128 ppm. Niobium concentrations are low, not exceeding 25 ppm. Zirconium concentrations, as in the shale matrix of drill core SLT-015, probably reflect accessory zircon grains; concentrations range between 100 and 285 ppm. Yttrium ranges in concentration from 47 to 114 ppm. Strontium concentrations range from 84 to 264 ppm. Molybdenum and uranium concentrations were measured but were all below the detection limit.

4.1.4. Geochemical comparisons between drill cores

The most abundant elements in the studied drill cores are Fe, Mn, Al, Si, Na and Ba in no particular order. The ferromanganiferous matrix of drill core SLT-015 is comparable in hand specimen to the ferromanganiferous ore of drill core SLT-017. However, a geochemical comparison of the rocks gives a different view. Figure 4.2 shows that Fe_2O_3 and MnO concentrations are higher in SLT-015 ferromanganiferous matrix than in SLT-017 ore. Also, the majority of samples in the ferromanganese matrix of SLT-015 contain a larger percentage of Fe_2O_3 than all the samples in drill core SLT-017. A broadly negative correlation of iron to manganese in the ferromanganiferous matrix of drill core SLT-015 is also illustrated in Figure 4.2.

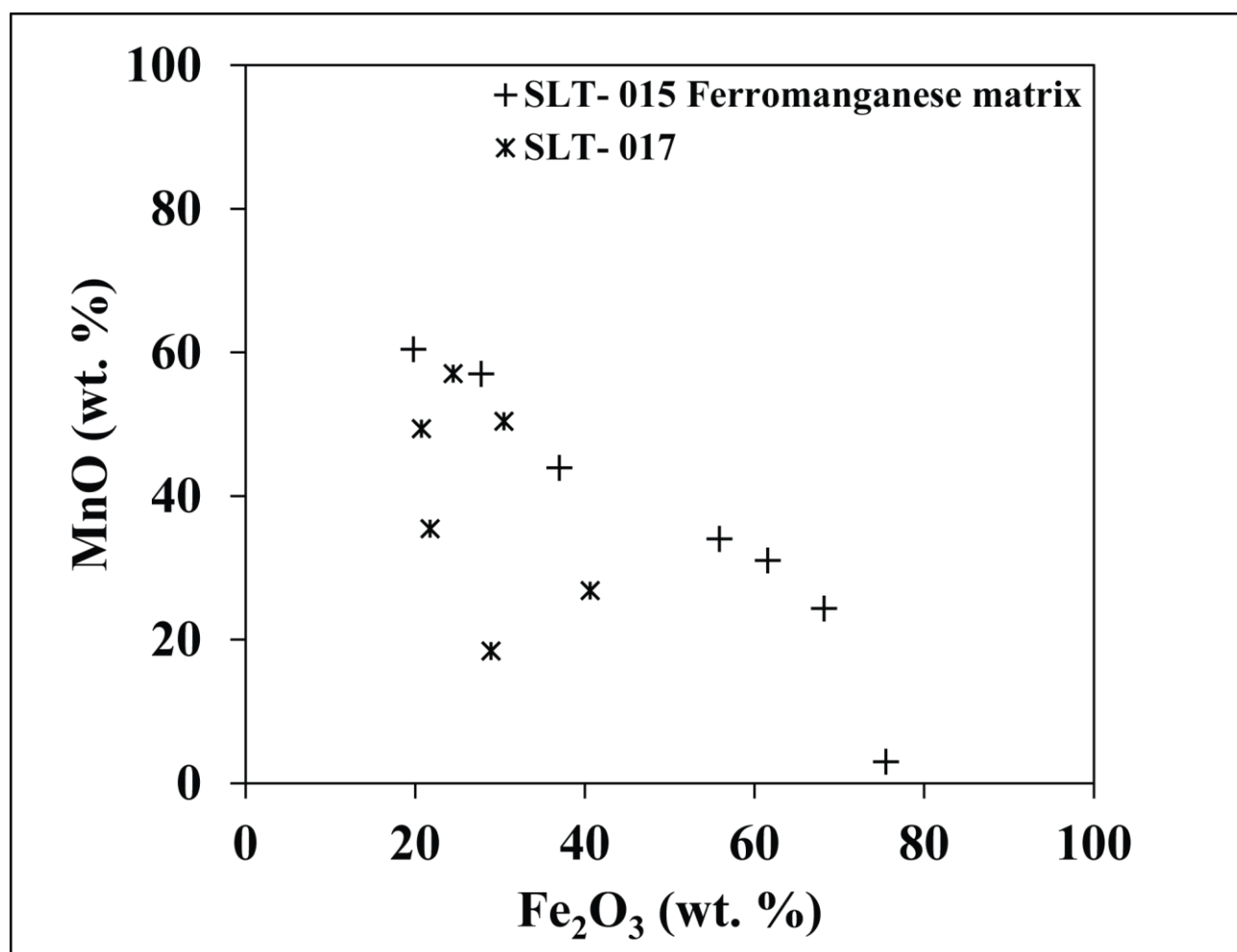


Figure 4.2: Fe_2O_3 versus MnO for ferromanganese matrix of drill core SLT-015 and the ferromanganese ore of drill core SLT-017.

As expected, the AKH-49 drill core, as well as the shale matrix of SLT-015, is depleted in Fe_2O_3 and MnO in comparison to the ferromanganese matrix in drill cores SLT-015 and SLT-017. The average concentration of SiO_2 is highest in drill core AKH-49 (54.71 wt. %) and the shale matrix of SLT-015 (35.38 wt. %). This is in contrast to the average SiO_2 concentrations in the ferromanganiferous matrix of SLT-015 (5.42 wt. %) and SLT-017 (11.56 wt. %). However, the ore in drill core SLT-017 is approximately twice as siliceous as the ferromanganiferous matrix in SLT-015.

The other major elemental constituents in all samples are Na, Al and Ba and these are represented in the ternary diagram shown in Figure 4.3. In this system, three distribution patterns can be identified. The first is that of the SLT-015 shale matrix which has the highest concentrations of Al_2O_3 in relation to Na_2O and BaO . The second is that of AKH-49 which also has high Al_2O_3 but also has a greater ratio of BaO to Al_2O_3 . There is one outlier in this second pattern which contains a higher proportion of Na_2O . The third is that of the high manganese and iron samples of SLT-015 and SLT-017 which show a broad overlap in Ba-Al-Na distribution. This distribution pattern has an even greater BaO to Al_2O_3 ratio. SLT-017 also has one outlier which has a much lower BaO to Al_2O_3 ratio compared to other samples within the third distribution pattern. Although all samples contain some Na_2O , the major factor controlling distribution in this system is the BaO to Al_2O_3 ratio.

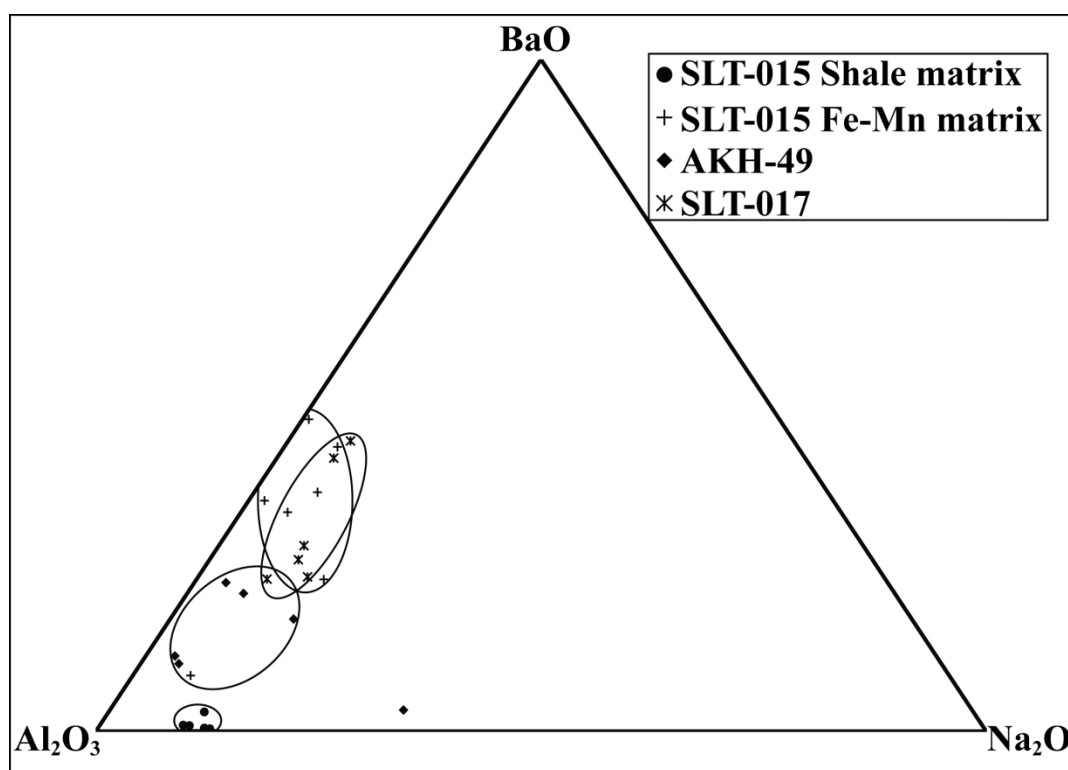


Figure 4.3: BaO- Al_2O_3 - Na_2O ternary diagram for all samples.

The high amounts of BaO, Na₂O and, in some cases (especially AKH-49), K₂O in these rocks may have various implications linking to the alteration or indeed, even the formation of the PMF ore deposits. These implications are addressed later, in the discussion of Chapter 5.

4.2. Trends and Correlation

This section aims to highlight geochemical trends and relationships that exist within the bulk rock geochemical. In SLT-015 two units are identified: shale matrix and ferromanganiferous matrix. Element trends within SLT-015 can be unit-specific or propagate across both units. In the shale matrix of SLT-15 a positive correlation exists between vanadium and iron as shown in Figure 4.4.

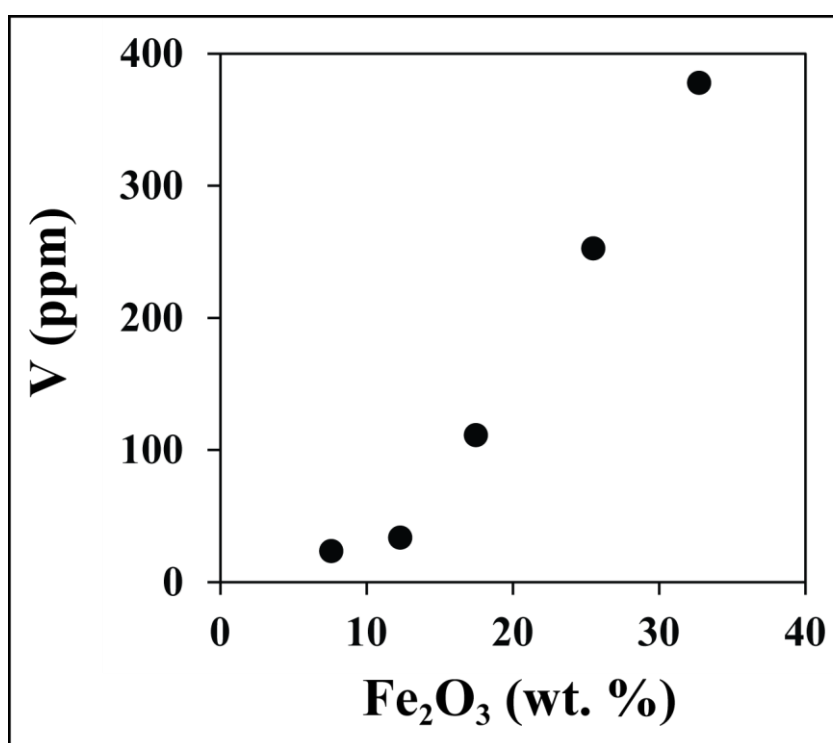


Figure 4.4: Positive correlation of Fe₂O₃ *versus* V in the shale matrix of SLT-015.

One outlier exists in Figure 4.4. The correlation coefficient with this outlier included is 0.986. When the outlier is removed in the calculation, the correlation coefficient becomes 0.999. This suggests that vanadium is substituting for iron in iron-bearing phases. The fact that a trend line would not run through the origin suggests the involvement of more than one iron-bearing phase.

Other correlations exist within the shale matrix unit of SLT-015 but these correlations are also reflected when data from the ferromanganiferous matrix is included. This is shown in Figure 4.5. The strong positive correlations exhibited by SiO_2 versus Na_2O (0.972), Al_2O_3 (0.989) and loss on ignition (L.O.I) (0.892) suggest that there are one or more Na-Al-bearing, hydrous silicates responsible for controlling the amount of mineral water in the bulk rock samples in drill core SLT-015. Paragonite, already described in Chapter 3 of this thesis, is present in SLT-015 and is one such silicate. In the ferromanganese matrix it is likely that this mineral occurs as minor, extremely fine-grained aggregates.

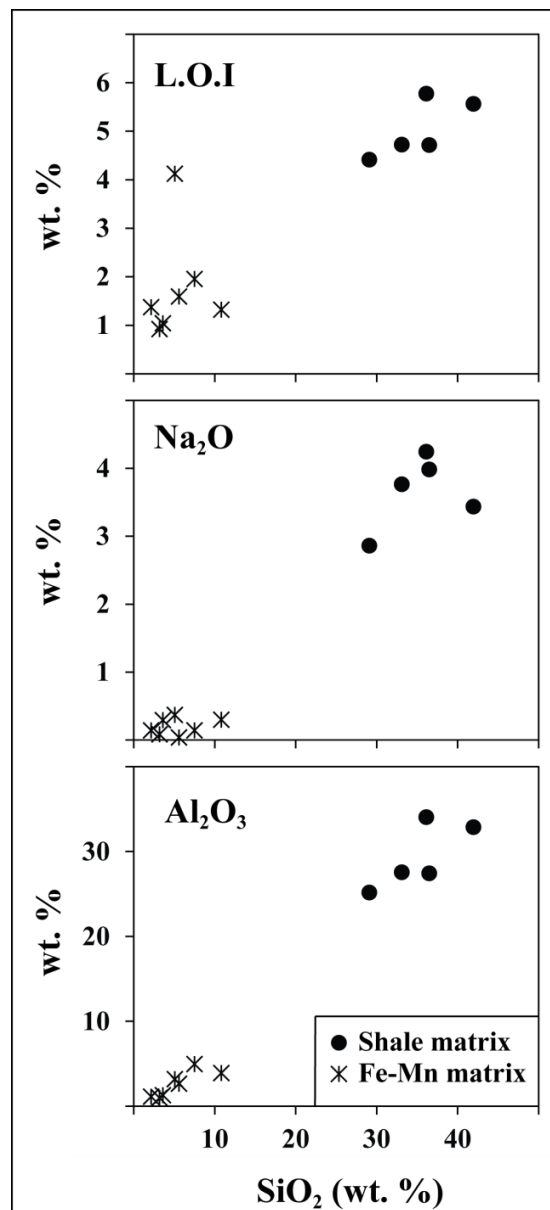


Figure 4.5: Harker variation diagrams for the shale and ferromanganiferous matrix in drill core SLT-015.

A low-resolution chemostratigraphic plot of absolute concentrations of Fe_2O_3 and MnO in the ferromanganese matrix of drill core SLT-015 is given in Figure 4.6. This figure shows that the two oxides have an antithetic relationship in this unit. Furthermore, MnO concentrations show a general increase with decreasing depth in the core whereas Fe_2O_3 concentrations decrease upwards. Such trends do not exist in the ferromanganese ore of SLT-017. The mineralogy of the ferromanganese matrix also reflects this stratigraphic trend with hematite having a higher modal abundance at the base of SLT-015 than braunite.

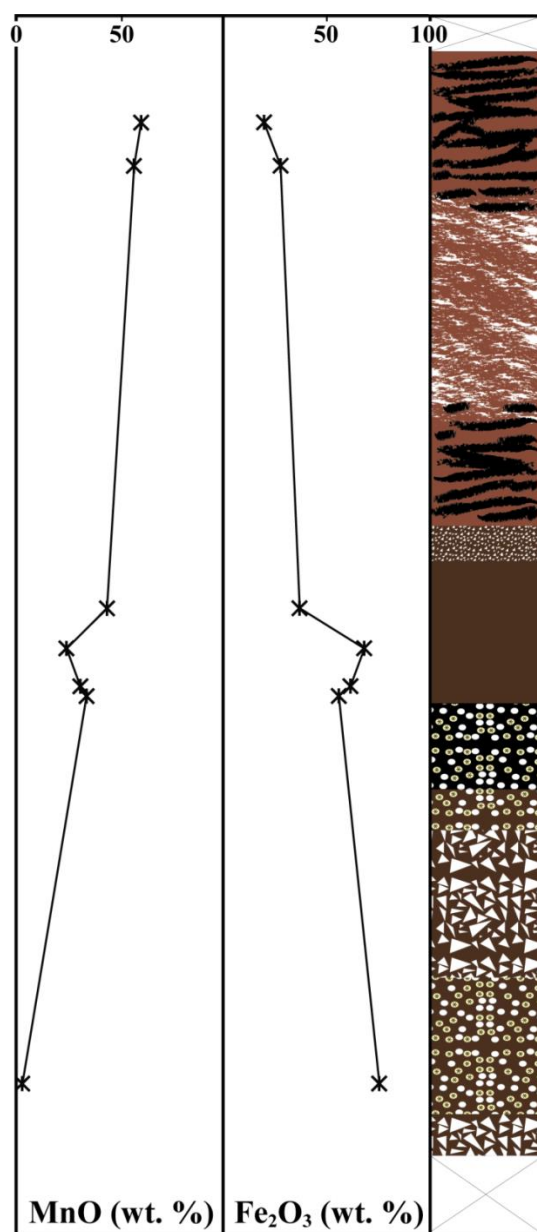


Figure 4.6: Variation diagrams of Fe_2O_3 and MnO concentrations with depth from ferromanganiferous matrix in drill core SLT-015. Stratigraphic log of SLT-015 is provided for reference.

Drill core SLT-017 contains various elements that correlate positively with SiO_2 . These positive correlations are presented in Figure 4.7. Na_2O and Al_2O_3 correlate positively with SiO_2 . The correlation coefficients are 0.989 and 0.997 respectively. Interestingly, save for two outliers, a positive correlation also exists in Si-Ba space. The correlation coefficient in this instance is 0.676 when the outliers are included and 0.996 when they are removed. Banalsite has been identified through microprobe and XRD analysis in SLT-017 and the correlations can be explained by the presence of this phase. The data plots close to the dashed line which represents the ideal stoichiometry of banalsite in SiO_2 versus BaO space. In the case of the outliers in Si-Ba space, it is possible that these samples contain other barium phases such as witherite and/or barite.

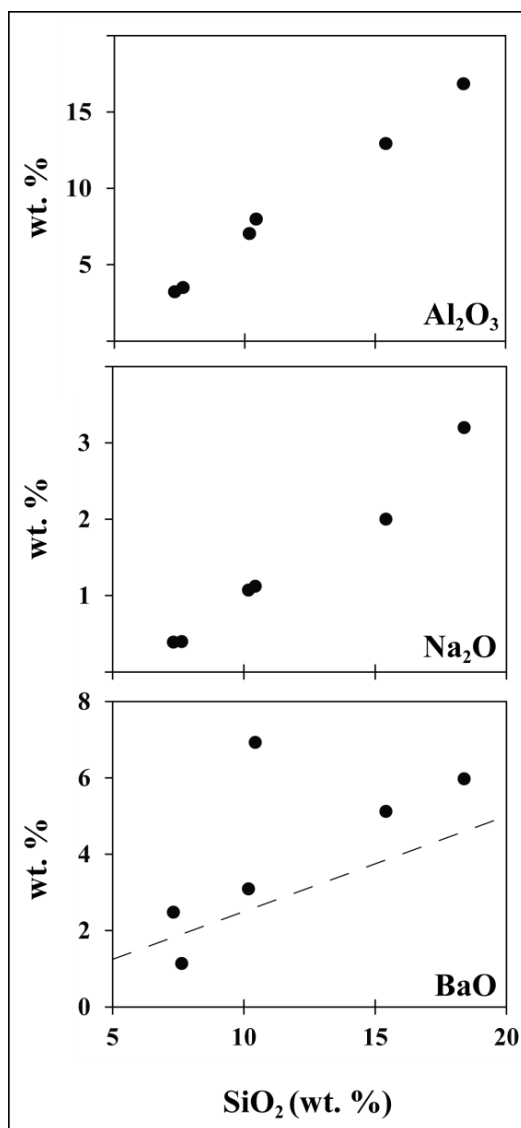


Figure 4.7: Selected Harker variation diagrams for the ferromanganiferous ore of drill core SLT-017. The dashed line corresponds to the ideal stoichiometry of banalsite.

Across all three drill cores positive correlations exist between particular elements. These correlations are illustrated in the variation diagrams shown in Figure 4.8. The correlation between SiO_2 and Al_2O_3 applies to SLT-015 and SLT-017 but not to AKH-49. This suggests that the aluminium and silicon in SLT-015 and SLT-017 can be accounted for by the presence of aluminium-bearing silicates. However, the greater concentrations of SiO_2 relative to Al_2O_3 in AKH-49 suggest an abundance of quartz in these samples. The Rb-K correlation across all samples is indicative of Rb concentrations being a function of the abundance of K-bearing phases in the samples as Rb readily substitutes for potassium.

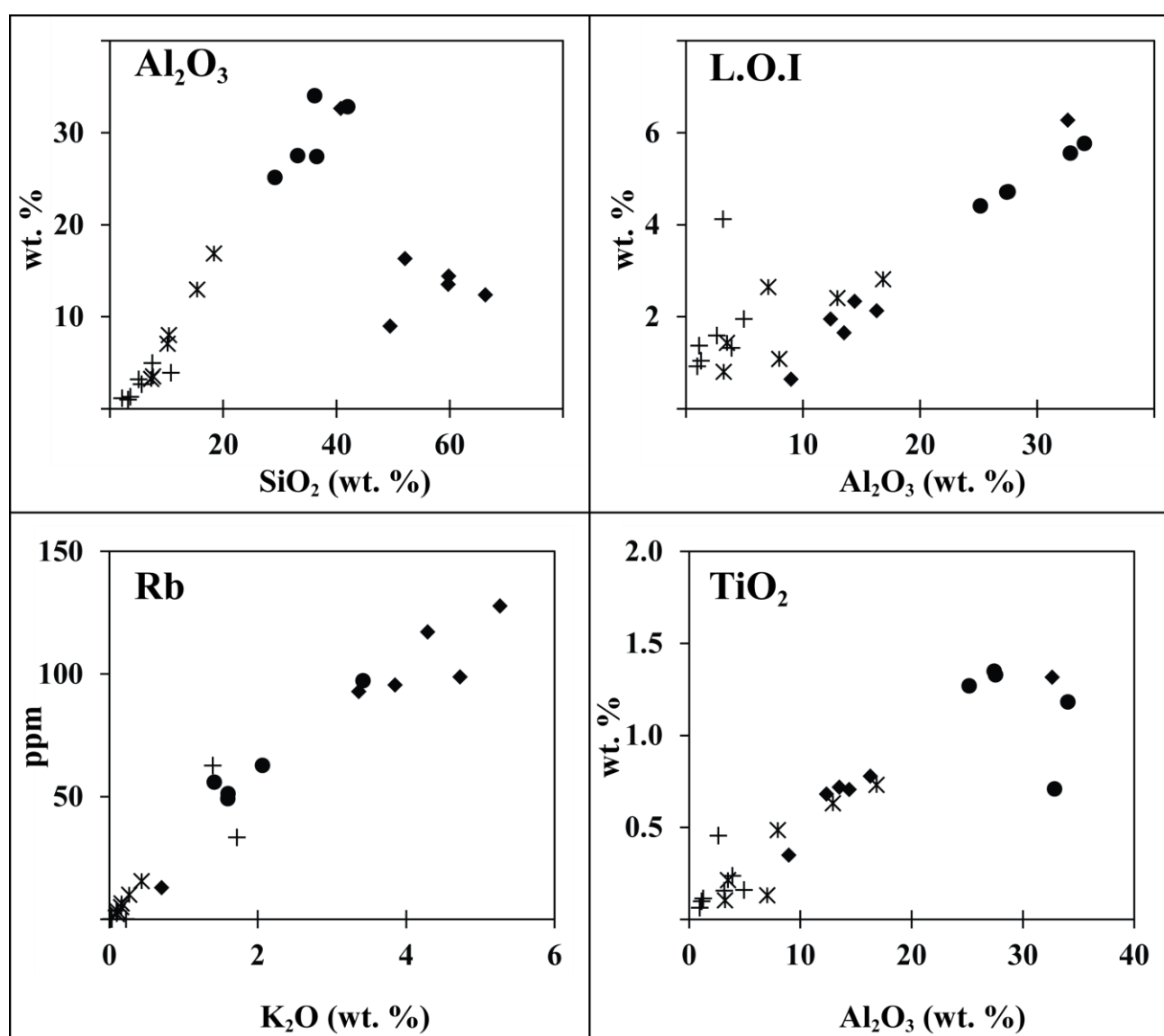


Figure 4.8: Variation diagrams of selected elements in drill cores SLT-015, SLT-017 and AKH-49. Key: Dots = SLT-015 shale matrix; Crosses = SLT-015 ferromanganiferous matrix; Diamonds = AKH-49; Asterisks = SLT-017.

The positive correlation between TiO₂ and Al₂O₃ concentrations in all the drill cores is indicative of a detrital source for these elements. Therefore, the positive correlation between SiO₂ and Al₂O₃ would suggest that silicon is also of detrital origin. This further suggests that all samples have a shale component – even the Fe-Mn ore samples in drill core SLT-015 and SLT-017.

4.3. **Stable isotope geochemistry**

4.3.1. Oxygen isotope data for braunite

Stable isotopes are useful in the determination of the nature of fluid-rock interactions (Baumgartner and Valley, 2001). Oxygen isotopic compositions are usually expressed in terms of the variation in the ¹⁸O/¹⁶O ratio (i.e. δ¹⁸O) (Allègre, 2008). In this study, the conventional representation of oxygen isotope variations is used and is expressed by:

$$\delta^{18}\text{O}_{\text{mineral}} = 10^3 * [({}^{18}\text{O}/{}^{16}\text{O})_{\text{mineral}} - ({}^{18}\text{O}/{}^{16}\text{O})_{\text{VSMOW}}] / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{VSMOW}},$$

where VSMOW is the Vienna Standard Mean Ocean Water of Gonfiantini (1978).

Difficulties arise when experimental data is not available for the mineral/s that are analysed. Unfortunately, very little published data exists for stable isotopic data of braunite. The oxygen isotopic composition of braunite has been determined by Bühn *et al.* (1995) in metamorphosed mangiferous chemical sediments in Namibia. Bühn *et al.* (1995) also point out that no oxygen isotopic experimental data exist that determine the fractionation capacity of braunite. Currently, to the author's knowledge, there still have not been stable isotope experiments performed on braunite. Bühn *et al.* (1995) used the increment method, a method described by Hoffbauer *et al.* (1994) to determine theoretical oxygen isotope fractionation factors between mineral pairs. However, in this study, the oxygen isotope fractionation considerations of interest have to be confined between braunite and water, as no other minerals were analysed for oxygen isotopes.

Table 4.5 shows the oxygen isotopic compositions obtained from analysis of 6 braunite separates from the ferromangiferous matrix of drill core SLT-015. The unit from which these braunite samples were obtained predominantly consists of euhedral, coarse-grained braunite. The δ¹⁸O values

range from 2.9 to 3.99 ‰. The theoretical yield for braunite was calculated on the basis of the formula for the average braunite in SLT-015 which is: $\text{Mg}_{0.01} \text{Mn}^{2+}_{0.8} \text{Ca}_{0.16} \text{Fe}^{3+}_{0.23} \text{Al}^{3+}_{0.09} \text{Mn}^{3+}_{5.74} \text{Si}_{0.98} \text{O}_{12}$. The result is a theoretical yield of 10.22 $\mu\text{mol/mg}$. Thus the percentage yields range from 98.43 – 104.31 %.

Table 4.5: Oxygen isotopic composition of six braunite separates from the ferromanganiferous ore of SLT-015.

Sample Number	$\delta^{18}\text{O}$ (‰) VSMOW	Absolute Oxygen yeild ($\mu\text{mol/mg}$)	Oxygen Yield (%)*
15-15E br	2.9	10.42	101.96
15-15F br	3.95	10.06	98.43
15-15G br	3.31	10.16	99.41
15-15H br	3.99	10.26	100.39
15-15I br	3.17	10.41	101.86
15-15J br	3.54	10.56	103.33
15-15J br duplicate	3.44	10.66	104.31

*Percentage oxygen yield calculated using the calculated theoretical yield of average braunite in SLT-015 (10.22 $\mu\text{mol/mg}$)

The range of $\delta^{18}\text{O}$ values for braunite, as determined by Bühn *et al.* (1995) for the Otjosundu manganese formations, is 1.3 to 6.1 ‰ (Figure 4.9). The average $\delta^{18}\text{O}$ value, however, is approximately 4.3 ‰ which is similar to the average $\delta^{18}\text{O}$ value of hematite (5.0 ‰) determined by the same authors for the same suite of rocks. Given the similarity between the average values and the overlap of the ranges, it is plausible that hematite and braunite are behaving in a similar way in terms of oxygen isotope fractionation. Similar assumptions have been made by Hoefs *et al.* (1987) who determined the $\delta^{18}\text{O}$ of manganese oxides and hematite and showed the similarity between the values. However, the fact that braunite is essentially a silicate mineral must be taken into consideration when making such assumptions. In this light, hematite $\delta^{18}\text{O}$ from Sishen iron ores nearby, ought to have recorded comparable values to the braunites from this study, if the fluids responsible for ore formation in both instances shared a common source. The fact that they do not compare well suggests possibly diverse fluid origins of the ores.

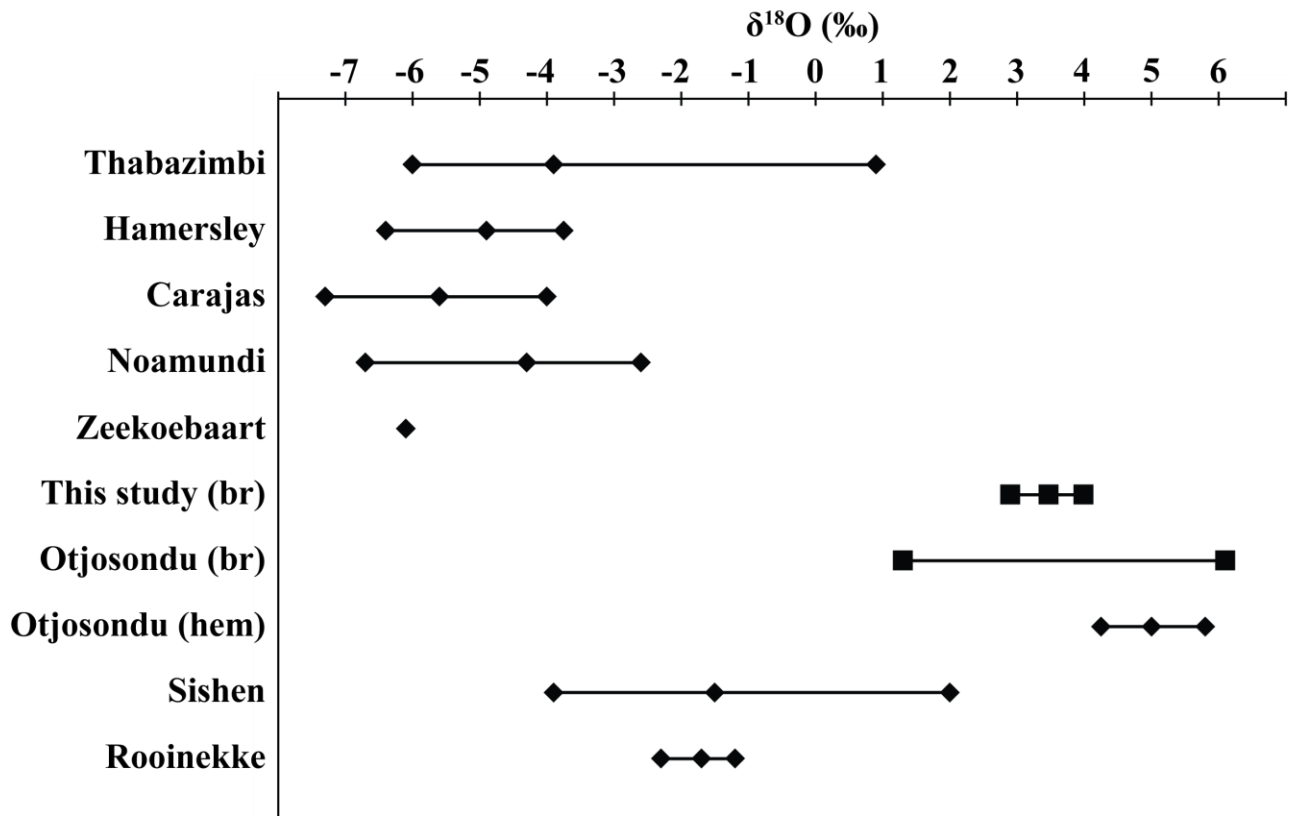


Figure 4.9: Ranges of hematite and braunite $\delta^{18}\text{O}$ values for various iron/manganese ore deposits. The central data marker in each range represents the average value and all data is for hematite unless otherwise stated (Modified after Gutzmer *et al.*, 2006).

4.3.2. Carbon and oxygen isotope data for dolomite

The oxygen isotope data in this section is reported as described in section 4.3.1. The data in this section is reported using the conventional method for presenting carbon isotope variations, that is, as $\delta^{13}\text{C}$ values. This is defined by the following equation:

$$\delta^{13}\text{C}_{\text{mineral}} = [({}^{13}\text{C}/{}^{12}\text{C})_{\text{mineral}} - ({}^{13}\text{C}/{}^{12}\text{C})_{\text{PDB}}] / ({}^{13}\text{C}/{}^{12}\text{C})_{\text{PDB}},$$

where PDB stands for Pee Dee Belemnite (Hoefs, 1987).

The carbon and oxygen isotope data in this section is derived from bulk-rock dolostone samples from Campbellrand Subgroup rocks immediately below the Wolhaarkop breccia in drill core SLT-018. Table 4.6 shows this data.

Table 4.6: Oxygen and carbon isotopic compositions of dolomite from the Campbellrand dolostones in drill core SLT-018.

Sample number	$\delta^{18}\text{O}$ (‰)	$\delta^{13}\text{C}$ (‰)
	VSMOW	PDB
18-13	19.38	-0.70
18-15	18.52	-0.48
18-18	18.56	-0.52
18-19	18.31	-0.54

The $\delta^{18}\text{O}$ values for the dolomites range from 18.31 to 19.38 ‰. The $\delta^{13}\text{C}$ values range from -0.70 to -0.48 ‰. This range overlaps with the range for unaltered dolomites of the Campbellrand Subgroup as analysed by Fischer *et al.* (2009). This is shown in $\delta^{18}\text{O}$ vs. $\delta^{13}\text{C}$ space in Figure 4.9. The data from Fischer *et al.* (2009) is also in agreement with analyses performed on unaltered Campbellrand Subgroup dolomites by Beukes *et al.* (1990). Fischer *et al.* (2009) show that the $\delta^{13}\text{C}$ values in the Campbellrand Subgroup reflect the carbon isotopic composition of the ocean at the time of carbonate deposition. The $\delta^{18}\text{O}$ values of this study, overlapping those of the study by Fischer *et al.* (2009), reflect only minor alteration effects most likely associated with diagenetic processes (Fischer *et al.*, 2009). The depleted nature of $\delta^{13}\text{C}$ for carbonates of the Makganyene Formation bioherms and Mooidraai Formation calcite reflects the influence of organic matter (Tsikos *et al.*, 2001; Faurey *et al.*, 2013).

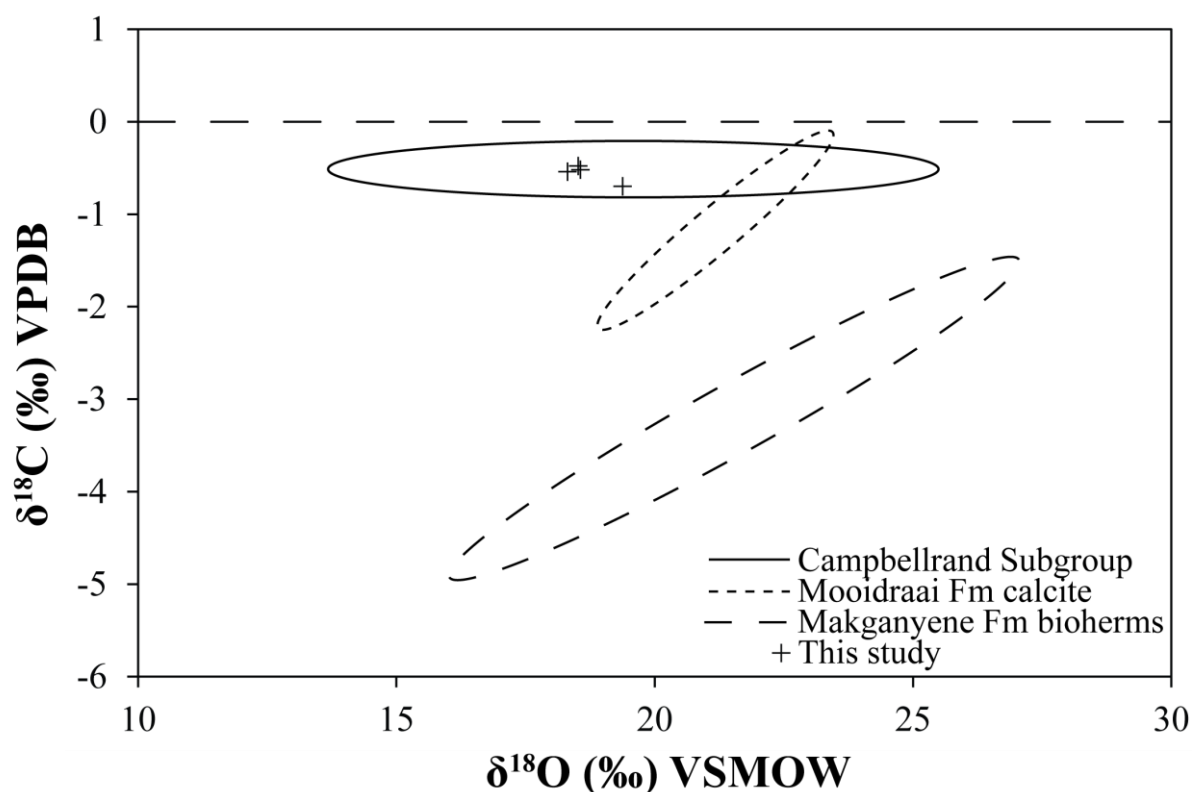


Figure 4.10: Carbonate $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ for Campbellrand Subgroup dolomites of this study, Campbellrand Subgroup carbonates (Fischer *et al.*, 2009), Mooidraai Formation carbonates (Tsikos *et al.*, 2001) and Makganyene Formation dolomitic bioherms (Fairey *et al.*, 2013).

4.4. Summary

The bulk rock geochemistry of these ores is complex. Iron and manganese are the most abundant oxides in SLT-017 and the ferromanganiferous matrix of SLT-015. The abundance of quartz in the matrix of AKH-49 is reflected by the high concentration of SiO_2 and the fact that this oxide does not correlate well with Al_2O_3 . The shale matrix of SLT-015 reflects the shale content by possessing high Al_2O_3 and SiO_2 as well as reflecting a detrital signature in the correlation of TiO_2 and Al_2O_3 . The fact that in all the studied drill cores Al_2O_3 correlates with L.O.I suggests the predominant Al-bearing minerals in the matrix are hydrous (e.g. paragonite). The barium content of these rocks is anomalously high with many samples having BaO content greater than 1 wt. %. Such enrichments of barium are likely to be allogenic. Anomalously high amounts of Pb, Sr and Cu are also present with some samples having over 1000 ppm for some of these elements.

Chapter 5

Discussion

The prevailing models for development of manganese ores in the Postmasburg manganese field invoke residual karst-forming processes in manganese-rich dolomites of the Campbellrand Subgroup (Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). The models proposed by Plehwe-Leisen and Klemm (1995) and Gutzmer and Beukes (1996a) differ for the two main types of deposits (i.e. siliceous and ferruginous ores).

Gutzmer and Beukes (1996a) consider the siliceous ores to have formed in cave systems developed under the Asbestos Hills BIFs. Plehwe-Leisen and Klemm (1995), however, regard the start of karstification to be before the onset of Asbestos Hills deposition. In terms of the nature of any fluids involved in this system, Plehwe-Leisen and Klemm (1995) suggest a descending meteoric fluid which evolves through the orebody as it descends, increasing in pH and decreasing in Eh. This develops an alkaline environment at the base of the karstic depression (Plehwe-Leisen and Klemm, 1995). Gutzmer and Beukes (1995) consider barian muscovite, aegirine and albite, which are present in the siliceous ores, to be of metamorphic origin. The presence of romanechite and cryptomelane results from the replacement of braunite under supergene conditions (Gutzmer and Beukes, 1996a). Both sets of authors thus pay little attention to the potential influence of hydrothermal fluids on ore formation and upgrading.

According to Gutzmer and Beukes (1996a), the ferruginous ores developed under surficial conditions as a result of lateritisation of the Reivilo Formation. Gutzmer and Beukes (1996a) support this interpretation by comparing observations made for the ferruginous ores with lateritic, karst-hosted wad deposits near Hesse, Germany. These observations include early diagenetic microconcretions and soft sediment deformation features as well as banded botryoidal aggregates. Gutzmer and Beukes (1996a) further suggest that the gradual conformable contact between the manganese ore and the overlying Gamagara Formation shales is evidence for a surficial environment of karstification (i.e. fresh water dissolution).

This discussion first presents the petrographic similarities between the PMF ores of this study and the manganese-rich sediments associated with the Wolhaarkop Breccia near the Bruce iron ore mine

as described by Moore *et al.* (2011). Furthermore, similarities are drawn to petrographic observations further north, in the KMF. The implications of such similarities, particularly for processes of deposition of gangue phases, are also discussed. The nature of implicated fluids is discussed as well as associated dissolution and precipitation mechanisms. Evidence used in determining the prevailing ore genesis models for the PMF is compared and scrutinized and a new model is suggested. Finally, the relevance of fluid flow in the PMF ores to iron ore formation is explored.

5.1. Evidence for large-scale fluid migration

This study shows the complex mineralogy of Postmasburg manganese deposits that are unaffected by supergene processes at least after the time of deposition of the Gamagara Formation. This complexity is shown in the presence of various barium-bearing and barium-rich phases as well as Na- and K-bearing silicates. Drill cores SLT-015 and AKH-49 are the most mineralogically complex of the studied drill cores. A comparative table shows the dominant gangue mineralogy for SLT-015, SLT-017 and AKH-49 as well as for the KMF (Table 5.1). A striking similarity exists between the cations present in the various mineral assemblages. The elements that are common to SLT-015, SLT-017 and AKH-49 are Na, Ba, K, Si, Fe, Mn and Al. The common minerals are braunite and hematite. Common minerals in SLT-015 and AKH-49, in addition to braunite and hematite, are aegirine, albite, K-feldspar, sérandite-pectolite, quartz, strontianite and witherite. As expected, these minerals are a reflection of the common elements. However, SLT-015 and AKH-49 also contain more exotic minerals such as armbrusterite, norrishite, kentrolite and sugilite in AKH-49 and natrolite, noélbensonite, piemontite and arsenotokyoite in SLT-015. Paragonite is common to SLT-015 and SLT-017. Banalsite is only found in SLT-017 and can account for the high barium in this ore. Gangue, void-filling phases in AKH-49 and SLT-015 also show textural similarities. The zoned nature of some vug fills is similar in both drill cores.

Table 5.1: Comparative table of mineral assemblages in manganese deposits of the PMF and KMF as well as near the Bruce iron ore mine.

Name	Formula	AKH-49*	SLT-015	SLT-017	KMF**
Aegirine	$\text{NaFe}^{3+}\text{Si}_2\text{O}_6$	X	X		X
Aegirine-augite			X		
Albite	$\text{NaAlSi}_3\text{O}_8$	X	X		X
Armbrusterite	$\text{Na}_6\text{K}_5\text{Mn}^{3+}\text{Mn}^{2+}_{14}[\text{Si}_9\text{O}_{22}]_4(\text{OH})_{10}\cdot 4\text{H}_2\text{O}$	X			
Banalsite	$\text{BaNa}_2\text{Al}_4\text{Si}_4\text{O}_{16}$			X	X
Barite	BaSO_4		X		X
Barytocalcite	$\text{BaCa}(\text{CO}_3)_2$		X		
Braunite	$\text{Mn}^{2+}\text{Mn}^{3+}_6\text{O}_8\text{SiO}_4$	X	X	X	X
Calcite	CaCO_3		X		X
Hematite	Fe_2O_3	X	X	X	X
Hollandite	$\text{Ba}(\text{Mn}^{4+}, \text{Mn}^{3+})_8\text{O}_{16}$		X		X
K-feldspar	KAlSi_3O_8	X	X		
Kentrolite	$\text{Pb}_2\text{Mn}^{3+}_2\text{O}_2(\text{Si}_2\text{O}_7)$	X			X
Natrolite	$\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot\text{H}_2\text{O}$		X		X
Noelbensonite	$\text{BaMn}^{3+}_2\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$		X		
Norrishite	$\text{KLiMn}^{3+}_2\text{Si}_4\text{O}_{12}$	X			
Paragonite	$\text{NaAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$		X	X	
Partridgeite	Mn_2O_3		X		X
Pectolite	$\text{NaCa}_2\text{Si}_3\text{O}_8(\text{OH})$	X	X		X
Piemontite	$\text{Ca}_2(\text{Al}, \text{Mn}^{3+}, \text{Fe}^{3+})_3(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$		X		X
Quartz	SiO_2	X	X		X
Serandite	$\text{NaMn}^{2+}_2\text{Si}_3\text{O}_8(\text{OH})$	X	X		X
Sericite		X			
Strontianite	SrCO_3	X	X		
Sugilite	$\text{KNa}_2(\text{Fe}^{3+}, \text{Mn}^{3+}, \text{Al})_2\text{Li}_3\text{Si}_{12}\text{O}_{30}$	X			X
Arsenotokyoite	$\text{Ba}_2\text{Mn}^{3+}[(\text{As}, \text{V})\text{O}_4]_2(\text{OH})$		X		
Witherite	BaCO_3	X	X		

* data from Moore *et al.* (2011) and this study.

** data from Gutzmer and Beukes (1996).

In some parts of SLT-015, euhedral braunite is found lining the boundaries of gangue-filled vugs. This is similar to that described by Gutzmer and Beukes (1996a) for both siliceous and ferruginous ore types. Gutzmer and Beukes (1996a) also describe the presence of apatite and barian muscovite in the siliceous ores but these are not present in any of the studied drill cores. Most notable, however, is the absence of supergene-related minerals from the studied drill cores. These minerals include romanechite, cryptomelane, pyrolusite, lithiophorite, ramsdellite and, rarely, goethite which are described as part of the mineral assemblage of siliceous ores (Gutzmer and Beukes, 1996a). The ferruginous manganese ores mainly consist of braunite, bixbyite and diasporite, amesite and ephesite

(Gutzmer and Beukes, 1996a). Supergene phases are also present in the form of romanechite, pyrolusite and lithiophorite (Gutzmer and Beukes, 1996a). The absence of a supergene mineral assemblage in the drill cores of the present study indicates the lack of recent supergene processes acting on the manganese ore in these drill cores. The presence of hollandite in SLT-015 is not necessarily indicative of supergene processes as it has also been found as a primary mineral in contact-metamorphosed manganese deposits (Anthony *et al.*, 2003).

Aegirine was previously reported in the PMF by De Villiers (1945) in association with albite. This study shows that these two minerals occur in the PMF in both the northern and southern extremities. Aegirine is also reported in the Hotazel Formation by Tsikos and Moore (1997). These authors postulate that the development of aegirine is as a result of sodic metasomatism of Hotazel Formation BIF by saline hydrothermal fluid flow. Strong evidence is provided by the authors in the form of cross-cutting quartz veins. These veins contain hematite with replacement rims of aegirine.

Cairncross *et al.* (2000) describe prehnite occurring in association with hydroxyapophyllite, datolite, inesite, calcite and pectolite from the N'Chwaning II mine in the KMF. Although no prehnite has been found in this study, the occurrence of natrolite is significant as it is known to be associated with prehnite (Cairncross *et al.*, 2000; Deer *et al.*, 1992). Cairncross *et al.* (2000) suggest that the occurrence of prehnite in the Wessels-type, high-grade manganese ores of the N'Chwaning II mine is potentially indicative of a hydrothermal overprint by low temperature (less than 250°C) fluids.

The abundance of sodium-bearing phases such as aegirine, albite, banalsite, natrolite and sérandite-pectolite of hydrothermal origin throughout the KMF and PMF suggests that hydrothermal activity did not occur on a localized scale but rather occurred on a regional scale as is also suggested by Moore *et al.* (2011). Identifying the conduit for such a regional flow remains challenging. However, two main geological features occur on a regional scale and are common to the PMF and KMF areas: these two features are the Black Ridge thrust fault and the unconformity between the Transvaal and Olifantshoek Supergroups. The timing of hydrothermal activity is also of importance; if an orogenic event was responsible for initiating fluid flow on a regional scale then two main events can be identified. The oldest possibility is that of the Kheis orogeny at around 1800 Ma (Moen, 2006). The other possibility is the Namaqua orogeny which took place between 1100 and 1050 Ma (Moen, 2006). Dixon (1989) dated sugilite from Wessels mine in the KMF which resulted in a Rb-Sr age of 1350 ± 269 Ma and a Pb-Pb age of 1270 ± 30 Ma. Gnos *et al.* (2003) also dated sugilite from Wessels mine using the $^{40}\text{Ar}/^{39}\text{Ar}$ technique which yielded an age of 1048.1 ± 5.9 Ma. Norrishite from Wessels mine was also dated by Gnos *et al.* (2003) but the results were not conclusive. Gnos *et*

al. (2003) interpreted the norrishite results in terms of two events: the first, at around 1010 Ma, represents the crystallization age of the norrishite; the second, at approximately 850 Ma, represents alteration of the norrishite to clay. Moore *et al.* (2011) dated sugilite from the Bruce mine in the northern part of the PMF using the $^{40}\text{Ar}/^{39}\text{Ar}$ technique. This yielded an age of 620.2 ± 3.3 Ma but Moore *et al.* (2011) pointed to a lack of confidence in the age as a result thermal overprinting causing a loss of radiogenic ^{40}Ar . Fairey *et al.* (2013), in an attempt to date undolomitised, unsilicified limestones of the Mooidraai Formation in the upper part of the Transvaal Supergroup, found that 4 discordant points formed a discordia line that yields a lower intercept age of 590 ± 63 Ma. Given these ages, in particular the sugilite ages, a postulated single regional hydrothermal event, as proposed by Moore *et al.* (2011), sometime toward the end of the Proterozoic is a realistic hypothesis. Obviously the ages do present a large range from 1350 Ma (Dixon, 1989) to 590 Ma (Moore *et al.*, 2011) and further research and dating of other hydrothermally deposited minerals in the region may better resolve this age range, and potentially unravel the events primarily responsible for ore-formation.

5.2. Nature of hydrothermal processes

5.2.1. Fluid characteristics

The lack of published fluid inclusion and stable isotope data from the Wolhaarkop breccia and associated manganese ores presents problems when trying to establish the nature of fluids that were responsible for depositing the broad assemblage of gangue minerals (and in some cases ore minerals) that can be found in these deposits. However, fluid inclusion studies have been performed in high-grade manganese ores of the KMF by Lüders *et al.* (1999) in hematite, hausmannite, calcite and datolite. Lüders *et al.* (1999) found that these minerals were deposited from high-salinity fluids with temperatures not exceeding 200°C.

The main Na-bearing phases in the studied drill cores are aegirine, albite, armbrusterite, sugilite and minerals of the sérandite-pectolite series (particularly the sérandite end-member). The blocky, euhedral nature of most of the albite in SLT-015 and AKH-49 suggests that this mineral was deposited hydrothermally in open space (Figure 5.1. A). Inclusion of sérandite in some albite grains may suggest crystallization of albite after sérandite. It is unlikely that any albite is detrital in origin

as firstly, it is difficult, given the surrounding geology, to provide a provenance for such grains. Secondly, there is no evidence of albite-bearing lithic fragments; any albite that occurs either occurs in masses of euhedral grains in vugs or lining vug walls or as individual euhedral grains. The lack of rounding in individual grains would further suggest authigenic formation of albite.

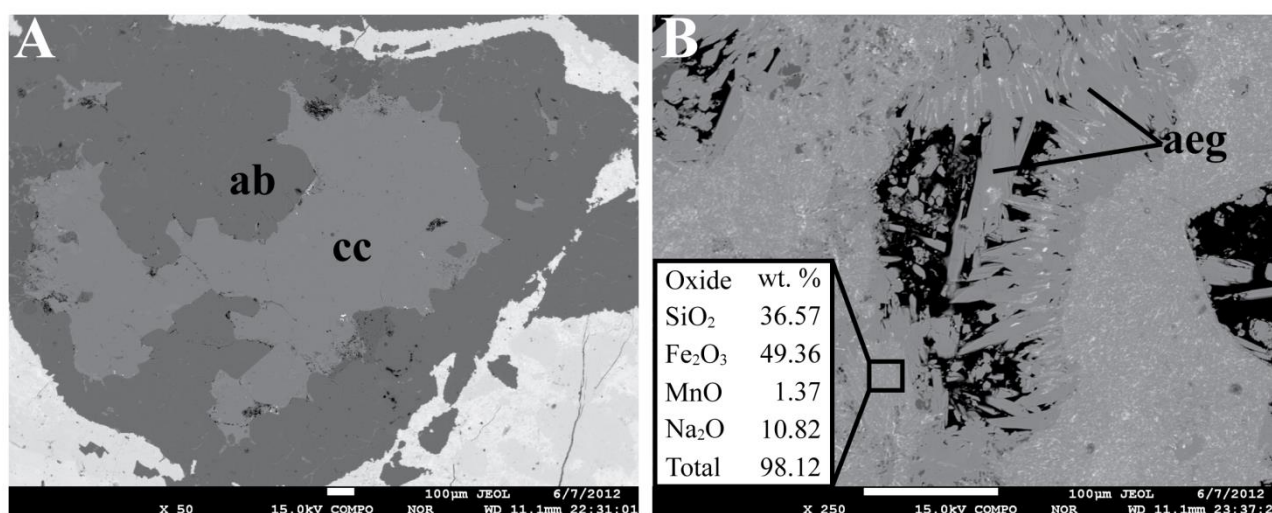


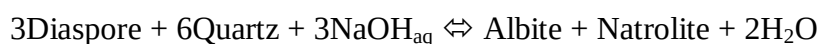
Figure 5.1: Backscattered electron images of some textures in SLT-015. **A.** Vug with albite growing from the walls as an outer rim with calcite forming the central core (sample 15-15E). **B.** Vugs in an aegirine-hematite matrix with aegirine laths growing from the vug walls (sample 15-15N). The inset shows key oxide composition of the matrix as analysed by a 10 μ m microprobe beam.

Aegirine occurs in abundance in small vugs in some parts of SLT-015. The aegirine laths grow outward from the vug walls as illustrated in Figure 5.1.B. The analysis of the matrix shows the large amount of sodium present. Using the average hematite and aegirine analyses presented in Chapter 3 it is possible to estimate the modal abundance of the matrix given the analysis in Figure 5.1.B. Assuming that almost all of the SiO₂ is assigned to aegirine, a modal abundance of 68% aegirine and 30 % hematite can be estimated for the matrix in this portion of the rock. The sérandite-pectolite series is also omnipresent throughout SLT-015 and AKH-49. This mineral group occurs throughout the Transvaal Supergroup stratigraphy where hydrothermal processes have played a role. The most abundant in SLT-015 and AKH-49, however, is sérandite, the Mn end-member. It is seen throughout drill core SLT-015 in vugs and also as pseudomorphous replacements of quartz. In both AKH-49 and SLT-015 sérandite tends to occur as radial aggregations but can also be found as laths.

Natrolite occurs in parts of drill core SLT-015. This zeolite phase either occurs as fine-grained rims on the walls of vugs in association with albite $\pm$ sérandite $\pm$ quartz or completely filling smaller vugs. Less hydrous zeolites such as natrolite, analcime, gonnardite and wairakite are stable at higher temperatures than those zeolites with higher water content such as clinoptilolite and stilbite (Sheppard and Hay, 2001). One possible explanation for the presence of natrolite in the manganese ore is the alteration of albite in the presence of water as given in the following equation:



However, this does not fit texturally as there is little or no quartz where natrolite is associated with albite. Also, some vugs are completely filled by natrolite only. Gutzmer and Beukes (1996a) point to the existence of diaspore in shale lenses in the ferruginous ores of the Western Belt. If it is assumed that diaspore is present at the time of influx of a Na-rich fluid then it follows that both natrolite and albite can be deposited in vugs as shown in the equation below:



The second scenario seems to better explain the textures found in drill core SLT-015.

In addition to these Na-rich phases, drill core AKH-49 contains vug-filling phases that are Na- and K-bearing such as armbrusterite and sugilite as well as some microcline and norrishite. In drill core SLT-015, however the dominant, if not sole, potassic phase is microcline and no armbrusterite, sugilite or norrishite is present. This is most likely to be a function of the availability of Li in the fluid at the time of deposition or perhaps a function of the level of silica saturation. The microcline in SLT-015 has an adularia-like habit. Figure 5.2 illustrates the typical habit of microcline in SLT-015. Here it occurs in association with sérandite-pectolite minerals as vug-fills. This habit is typical of potassium feldspars crystallizing from a hydrothermal solution (Deer *et al.*, 1992). Steiner (1970), in a study of an active geothermal system, showed that adularia can form in temperature conditions of less than 265°C.

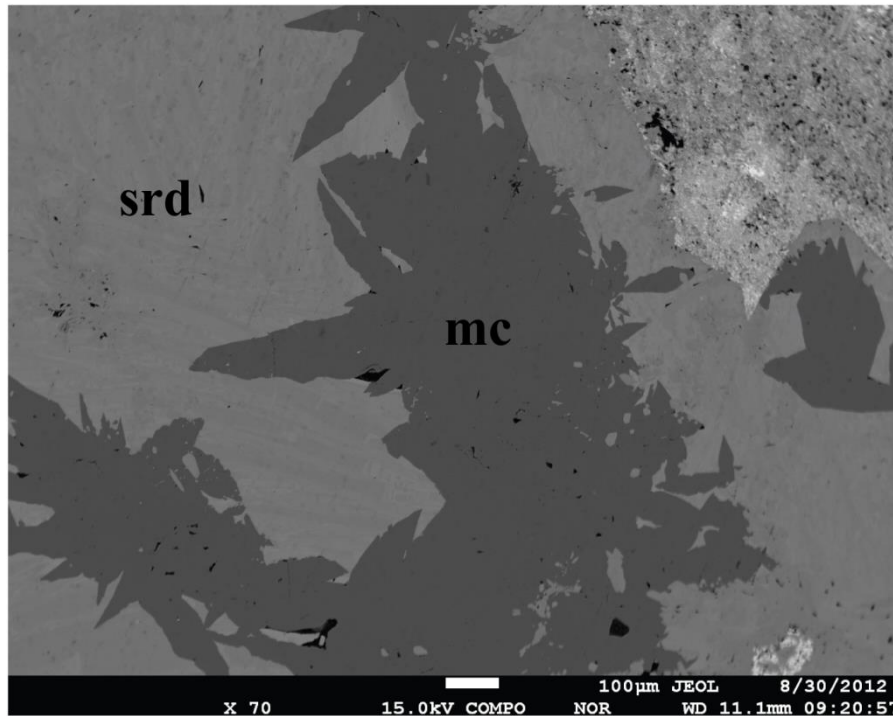


Figure 5.2: Adularia habit of microcline in drill core SLT-015 as an indicator for hydrothermal processes (sample 15-150).

Ca-, Ba- and CO₂-rich phases are also present in these drill cores. Coarse-grained calcite occurs as the central core of some vugs in drill core SLT-015 (Figure 5.1.A). Minor piemontite is also present lining the walls of small quartz-bearing vugs. A number of barium species exist in these rocks, particularly in drill core SLT-015. Witherite is the most abundant barium phase, commonly occurring as coarse, euhedral grains. This mineral is also found in drill core AKH-49. Barite is present in these drill cores, but not in great abundance. The presence of barium silicates such as noélbensonite and banalsite is also of interest. Noélbensonite, reported here as the first African locality, is found in drill core SLT-015. Replacement of microcline by noélbensonite and replacement of sérandite by witherite, arsenotokyoite and noélbensonite, is suggestive of late deposition of barium in a hydrothermal system. At the Woods mine, Australia, the type locality of noélbensonite, this mineral replaces sérandite amongst other Mn-bearing minerals (Kawachi *et al.*, 1996a). Kawachi *et al.* (1996a) interpret such replacement as a result of the activity of relatively low temperature Ba-bearing fluids that infiltrated after the metamorphic thermal maximum that produced sérandite. However, Armbruster *et al.* (1993) report hennomartinite, a structural relative of noélbensonite, at Wessels mine, South Africa, where the mineral precipitated in veins cogenetically

with sérandite-pectolite and sugilite. The abundance of banalsite in SLT-017 can account for almost all of the barium present in these rocks. An approximation of modal abundance using one of the bulk rock major element analyses from drill core SLT-017 gives modal compositions of 30 % hematite, 26 % banalsite, 22 % braunite, 12 % paragonite and 4 % diasporite; this leaves 6 % unaccounted for with small amounts of each oxide remaining.

The occurrence of arsenotokyoite is the first occurrence of the brackebuschite group minerals that contains both arsenic and vanadium. Tokyoite proper is the Mn-analogue of gamagarite (Matsubara *et al.*, 2004) which was first described in the Postmasburg manganese field by De Villiers (1943). De Villiers (1943) linked the gamagarite to fluid activity but made no comment on the source of such a fluid. Nevertheless, the discovery of arsenotokyoite in this study to the south of the original gamagarite locality seems to indicate the activity of a V-, Ba-, and As-bearing fluid.

All of these minerals show textural evidence of hydrothermal processes either through the habit of the mineral itself (e.g. microcline adularia and vug-filling euhedral albite) or by showing some replacement relationship with other minerals (e.g. noélbensonite after microcline and sérandite). Furthermore, the presence of zoned vugs can best be explained by hydrothermal processes. Given this fact, it would appear that the fluid affecting the ore deposits of the PMF were rich in barium, potassium, calcium and especially sodium. Lithium, silicon, vanadium and arsenic also formed minor constituents of this alkaline fluid. Also, previous experimental and case-study work on many of the minerals mentioned above shows that fluid temperatures probably did not exceed ca. 250°C.

5.2.2. Mechanisms of mineral deposition and metasomatism

The process of metasomatism by such a fluid involves influx of the fluid through the ore bodies. Chapter 4 of this study shows that the aluminium and, to a large extent, the silicon is of autotochthonous detrital origin. Dove and Nix (1997) show that the ability of water to dissolve quartz is increased with the addition of Mg^{2+} , Ca^{+} , Na^{+} , K^{+} and particularly Ba^{2+} . These experiments provide an elegant means to present a model for the formation of the gangue assemblages associated with the PMF ores. The experiments were conducted at 200°C – a temperature that is probably not unlike the one for the fluid which affected the PMF ores. As in the experiments conducted by Dove and Nix (1997), it is likely that the metals were mainly carried as chloride salt solutions or perhaps as hydroxides. This oxidized, high pH fluid interacted with quartz/chert clasts in the Wolhaarkop

breccia thus bringing SiO_2 into solution. During this process it is also likely that manganese and iron were mobilized at least on a local scale. At some point during quartz dissolution the fluid became supersaturated in silicon and lost its carrying capacity. The mode of crystalline SiO_2 in the rock determined the shape of the vug that would develop. Therefore, if the fluid dissolved chert then the vugs would be irregular in shape but if polygonal, coarse-grained quartz was dissolved then the vug would have a definite shape and it would appear as if minerals within them were pseudomorphously replacing quartz.

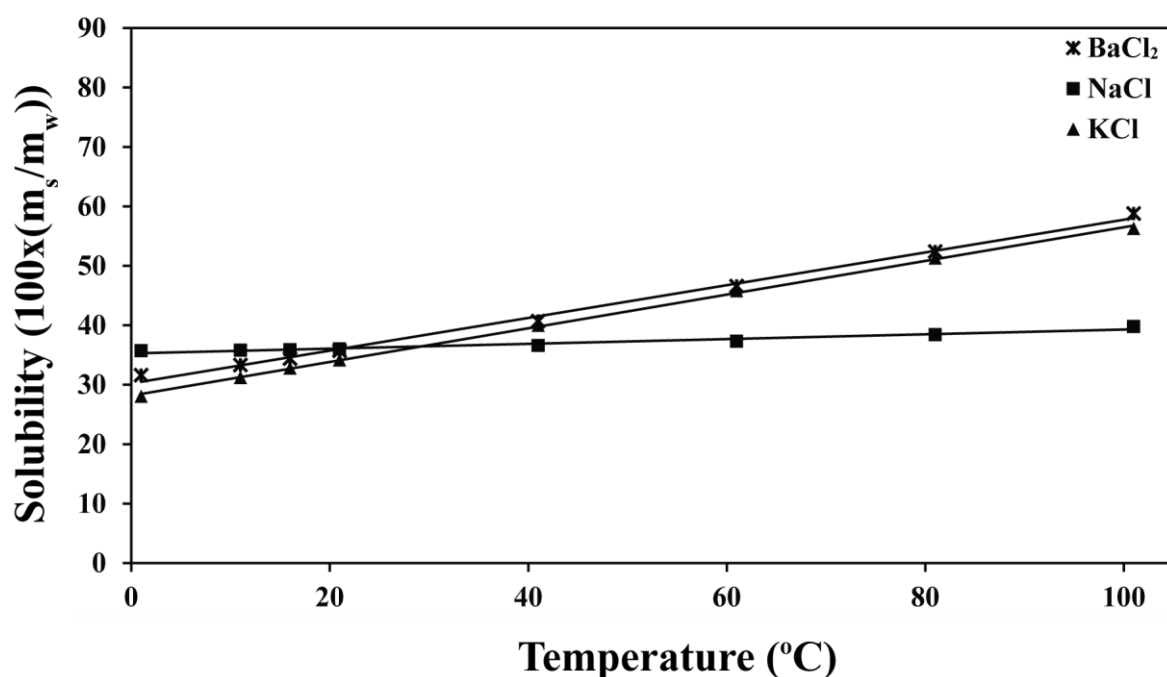


Figure 5.3: Solubility of BaCl_2 , NaCl , KCl in water as a function of temperature (experimental data from Kaye and Laby, 1995). Key: m_s = mass of the solute; m_w = mass of water.

Figure 5.3 shows the solubility curves for BaCl_2 , NaCl and KCl in water. The solubility of these chlorides increases linearly with increasing temperature. BaCl_2 and KCl behave similarly with BaCl_2 being more soluble than KCl . NaCl is much less soluble than the other two chlorides. Given these linear trends it is unlikely that the behaviour of these chlorides would change at elevated temperature (ca. 150-200°C). Of course, one would also need to consider other factors such as composition, Eh and pH of the fluid in order to gain a complete understanding of mechanisms of precipitation.

	Detrital	Diagenetic	Low-grade Metamorphic	Hydrothermal
Chert	██████████			
Quartz		██████████	■■■■■■■■■■	■■■■■■■■■■
Braunite		■■■■██████████	██████████	██████████
Hematite		■■■■██████████	██████████	██████████
Partridgeite			██████████	██████████
Aegirine				██████ ■
Aegirine-augite				██████ ■
Serandite-pectolite				██████ ■
Albite				■ █████
Natrolite				■ █████
Microcline				■■ █████ ■■
Sugilite				■■ █████ ■■
Armbrusterite				■■ █████ ■■
Arsenotokyoite				████
Barite				████
Noelbensonite				████
Witherite				████
Calcite				████

Figure 5.4: Paragenetic chart of the major ore and gangue mineral constituents in the studied drill cores.

Figure 5.4 illustrates the most likely paragenesis for the major mineral phases found in the ores of the PMF. Chert is of detrital origin. Polyhedral, authigenic quartz is likely to be of diagenetic origin as a result of recrystallization of chert and remobilization of silica and deposition in open spaces. Braunite and hematite formed during the diagenesis and low-grade metamorphism of residual ferromanganiferous wad. Given that NaCl is the least soluble of the major element constituents of the fluid, Na-rich minerals began to precipitate, reacting with available aluminium in the matrix to form albite and natrolite. Also, reaction of the fluid with the surrounding ferromanganiferous matrix

allowed for the precipitation of aegirine and sérandite as these minerals were able to scavenge iron and manganese. The development of aegirine almost exclusively along vug walls supports such a hypothesis. Furthermore, where albite occurs in zoned vugs, it seemingly always occurs as the outermost zone along vug walls, indicating that it was one of the earliest to be deposited. However, the occurrence of sérandite as an inclusion in albite and natrolite suggests that sodic phases that contain manganese or iron were deposited before the aluminous phases.

Where natrolite is found replacing fractured quartz it is likely that incomplete dissolution of the original coarse-grained quartz occurred. Potassium is the next least soluble and would thus follow after the deposition of sodium. The similarity in the solubility curves of BaCl_2 and KCl suggests that Ba and K should precipitate together. However, it is possible that the available reactants already present in the rock are more conducive for the formation of K-bearing phases than for Ba-bearing phases. The deposition of potassium is reflected in microcline in SLT-015 which, like albite, tends to grow from vug walls. However, the zonation of K-bearing phases is better seen in AKH-49 where masses of sugilite and/or armbrusterite occur in the inner core of zoned vugs (Moore *et al.*, 2011). The replacement of microcline and sérandite by Ba-bearing phases indicates that barium was the next element to precipitate out of solution. Therefore noélbensonite and witherite were deposited – this occurred in a replacive manner in some instances. In order to deposit arsenotokyoite at the same time, vanadium and arsenic must have also precipitated out of solution. Finally, any excess SiO_2 would be deposited in the inner part of zoned vugs as quartz.

In terms of fluid flow affecting ore minerals, evidence exists for replacement and recrystallization processes. The replacement of gangue phases by braunite is evident in one unit of SLT-015. It is likely that manganese, being mobilized on a local scale as MnCl_2 (which is more soluble than BaCl_2 [Kaye and Laby, 1995]) was precipitated later than barium in the hydrothermal system. This would explain the replacement of hydrothermal gangue phases by braunite. Hematite shows various recrystallization textures but this can also be linked to low-grade metamorphism. Where hematite ovoids exist in the ferromanganese matrix of SLT-015, many of these have an outer rim of Mn-rich material which can be interpreted as replacement rims due to localised manganese mobility. The presence of hollandite in parts of drill core SLT-015 account for elevated barium concentrations in bulk-rock geochemical analyses of some samples. This mineral gives further evidence for the presence of a Ba-rich fluid percolating through these ores. It also attests to the instability of the Mn^{3+} cation in natural minerals.

Braunite $\delta^{18}\text{O}$ values for coarse (average of approx. 200 μm), crystalline grains from SLT-015 give an average of 3.47 ‰ for 7 analyses. The lack of experimental isotopic data for braunite makes interpretation of these values difficult. However, as discussed in Chapter 4, hematite seems to behave in a similar fashion to braunite. If this is the case then the heavy $\delta^{18}\text{O}$ values, being different to hematite from iron ores associated with supergene processes, shows that the manganese ores were affected by a different process (see Chapter 4). The difficulty of such an interpretation lies in the fact that the temperature during which isotopic exchange was taking place is difficult to constrain. The heavy $\delta^{18}\text{O}$ composition of the braunites may also represent a diagenetic signature. In this case it is possible that isotopic exchange may not have taken place between the hydrothermal fluid and the braunite. Unfortunately, the $\delta^{18}\text{O}$ composition of the braunite will likely remain enigmatic until experimental data becomes available.

The $\delta^{18}\text{O}$ compositions of the dolomites immediately below the Wolhaarkop breccia do not show obvious evidence for any hydrothermal alteration. Therefore fluid flow did not affect the Campbellrand Subgroup dolomites. The $\delta^{13}\text{C}$ compositions of these dolomites are consistent with other works (e.g. Beukes *et al.*, 1990; Fischer *et al.*, 2009) and reflect the isotopic composition of the ocean at the time of carbonate deposition.

5.3. Evaluation of existing prevalent models

Most models for the development of the PMF ore deposits recognize the role of the Campbellrand dolomites as a source of manganese (Nel, 1929; Du Toit, 1933; De Villiers, 1944; De Villiers, 1960; Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a). The models proposed by Gutzmer and Beukes (1996a) and Plehwe-Leisen and Klemm (1995) are the most elegant models as yet proposed for the formation of the PMF ore deposits. However, this section of the thesis points to some limitations in the models proposed by these authors.

Gutzmer and Beukes (1996a) argue that the Wolhaarkop chert breccia only occurs where upgraded Manganore Iron Formation has slumped into sinkholes within the Fairfield Formation. However, drill core SLT-015, analogous of siliceous ore and the Wolhaarkop chert breccia, shows that the overlying material need not be Manganore Iron Formation. In the case of SLT-015, the overlying material consists of shales and quartzites of the Mapedi Formation. Furthermore, Gutzmer and Beukes (1996a) as well as Plehwe-Leisen and Klemm (1995) indicate that the matrix of the

Wolhaarkop breccia becomes iron-rich and siliceous toward the top and manganese-rich toward the contact with the underlying Campbellrand dolomites. Drill core SLT-015 again shows that this is not necessarily the case with the matrix in this core becoming manganese rich toward the top and iron-rich and chert-rich toward the base.

The presence of cryptomelane and goethite in braunite-lined vugs as well as other supergene-related minerals such as lithiophorite and romanechite, as described by Gutzmer and Beukes (1996a) for siliceous ores, should not be considered typical of such deposits. Such phases are likely typical of deposits that are at or very close to the modern erosion surface and have been affected by geologically modern meteoric waters. When one compares the mineralogy of these near-surface deposits to those that are at 80 or more meters from the surface (i.e. the drill cores of this study), a distinct lack of supergene minerals is noticeable.

Given the fact that SLT-017 is overlain by ferruginous pebble conglomerate of the Doornfontein member it is reasonable to assume that the manganese ore in the drill core is of the ferruginous type of the Western Belt. However, unlike the typical gradual conformable contact between the ore and the overlying conglomerate as described by Gutzmer and Beukes (1996a), the ore of SLT-017 shows an abrupt contact with the overlying Doornfontein member. Also, the presence of quartz clasts that are replaced by braunite in the lower part of the Doornfontein member further suggests localized mobility of manganese due to hydrothermal fluid infiltration as discussed in the previous section of this chapter.

Plehwe-Leisen and Klemm (1995) do not give any bulk geochemical data in support of the models that they put forward for the development of the PMF ores. Gutzmer and Beukes (1996a) have the most comprehensive set of bulk geochemical data that has been compiled for the PMF ores. Some of the diagrams used for characterization of the PMF ores by Gutzmer and Beukes (1996a) differ when the data from the current study are included. One such diagram is shown in Figure 5.4, where data are plotted in elemental (Cu+Ni+Co)-Fe-Mn space (Gutzmer and Beukes, 1996a).

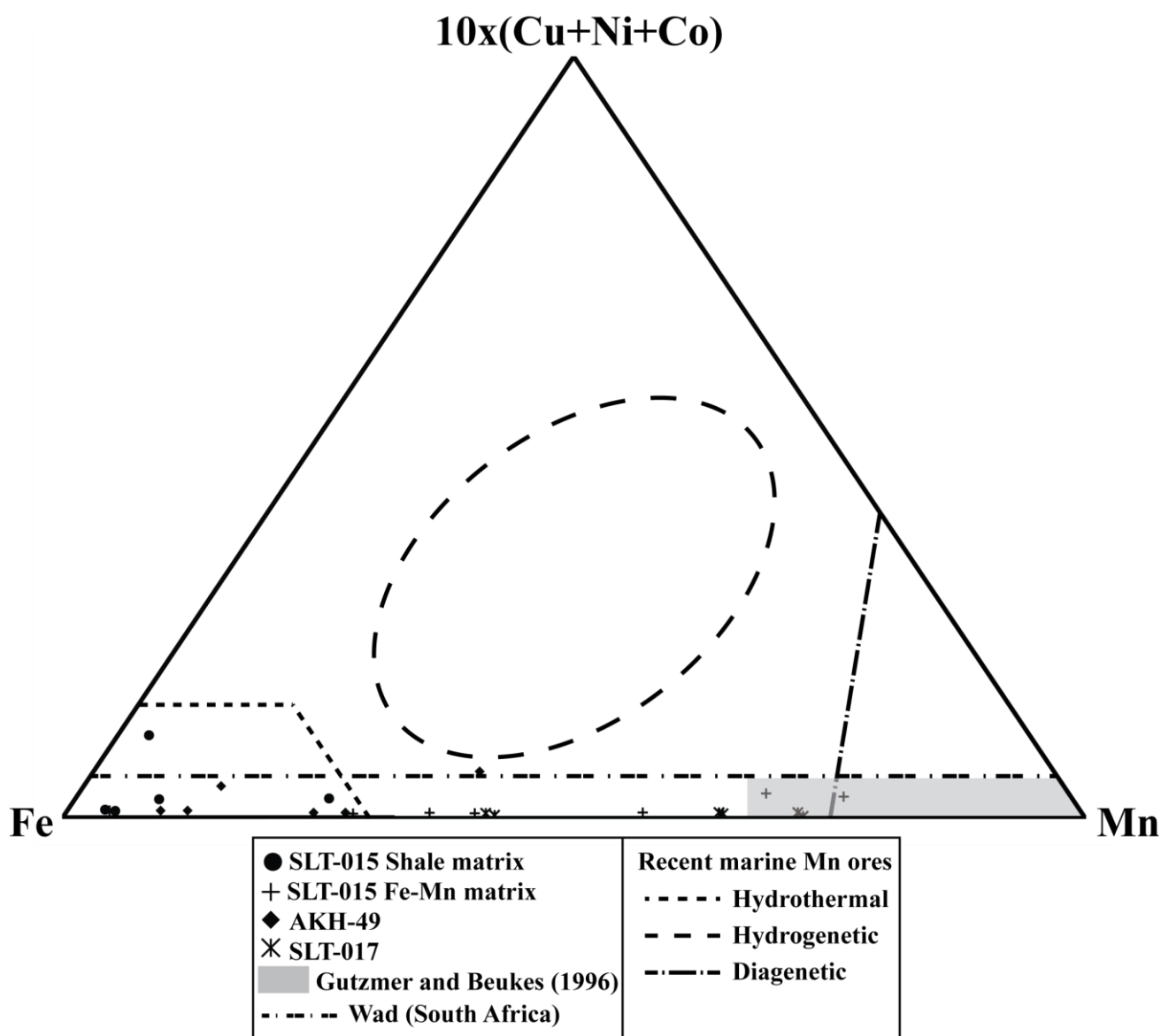


Figure 5.5: Bulk-rock geochemical data from this study and from Gutzmer and Beukes (1996a) plotted in (Cu-Ni-Co)-Fe-Mn space (Modified after Gutzmer and Beukes, 1996a).

The shaded area in Figure 5.4 represents data for siliceous and ferruginous ores as published by Gutzmer and Beukes (1996a). These authors stress the fact that the data coincide with recent South African karstic manganese wad deposits. However, these data also overlap with recent diagenetic marine manganese ore – this point is not addressed by Gutzmer and Beukes (1996a). Furthermore, only 4 samples from the ores of this study (i.e. SLT-017 and the ferromanganese matrix from SLT-015) coincide with the ores studied by Gutzmer and Beukes (1996a) with most ore samples occurring between hydrothermal and diagenetic recent marine manganese ores. Therefore, such diagrams are difficult to use in situations where a variety of processes acting upon the deposits greatly increases

their genetic complexity. Gutzmer and Beukes (1996a) record high barium (up to 4.86 wt. % Ba) in both siliceous and ferruginous ores. The authors account for such high barium by the presence of barite in some cases and supergene romanechite in others. This is not disputed in this thesis. However, it is interesting to note that in the drill cores of this study, apart from one sample which contains hollandite, the barium is not contained within these minerals but rather in witherite (in SLT-015 and AKH-49) and banalsite (in SLT-017). This attests to the barium-rich, generally sulphur-poor nature of the hydrothermal fluid.

Finally, the models proposed by both Plehwe-Leisen and Klemm (1995) and Gutzmer and Beukes (1996a) propose that the ores of the PMF were developed in the Fairfield and Reivilo Formations of the Campbellrand Subgroup. This is logical given the chert-bearing nature of the Fairfield Formation to form the Wolhaarkop breccia and given the chert-free, Mn-rich nature of the Reivilo Formation to form the ferruginous ores. However, a problem arises in the fact that these models do not account for the loss of approximately 800 m of dolomite represented by the Papkuil, Klippan, Kogelbeen and Gamohaam Formations which overly the Reivilo and Fairfield Formations. Such a loss would surely represent an erosional unconformity between the Campbellrand Subgroup and the overlying Asbestos Hills banded iron-formations. In addition, chert and manganese, as well as iron may have been derived from dissolution of those dolomite formations overlying the Fairfield Formation. Plehwe-Leisen and Klemm (1995) consider that an erosional period occurred before the deposition of the Asbestos Hills – this would account for the loss of the dolomites overlying the Fairfield Formation but would also suggest a regional unconformity between the Campbellrand Subgroup and the Asbestos Hills Subgroup.

The models proposed by Plehwe-Leisen and Klemm (1995) and Gutzmer and Beukes (1996a) for the formation of the ores of the PMF are robust for certain deposits, especially those affected by modern surficial processes. However, some shortcomings exist that pertain particularly to the variability of ores in the PMF, the impact of hydrothermal activity on the ores and the stratigraphic discrepancy. The model proposed in the following section aims to account for these shortcomings.

5.4. Processes of manganese ore formation in the Postmasburg Manganese Field: an all-encompassing model.

The ore deposits of the Postmasburg Manganese Field are stratigraphically, mineralogically and geochemically variable and complex. This must be accounted for when developing a genetic model for these deposits. There is little doubt that these deposits formed in karst environments and that the manganese, iron and the bulk of the silicon is derived from the dolomites of the Campbellrand Subgroup of the Transvaal Supergroup. However, to restrict the source of metals to the Reivilo and Fairfield Formations is to discount the overlying ca. 800 meters of dolomites which once overlay these formations.

The model presented incorporates the ideas of previous authors (i.e. Plehwe-Leisen and Klemm, 1995; Gutzmer and Beukes, 1996a) but envelops all deposit types into one model. It also tentatively provides a source of alkali metals for hydrothermal activity in the PMF. Figure 5.6 depicts this model. First, the dolomites of the Campbellrand Subgroup were deposited. These dolomites were then overlain by banded iron-formation of the Asbestos Hills Subgroup (known in the PMF as the Manganoir Iron-formation) (Figure 5.6.A). Tectonic activity led to the development of the regional anticlinal structure known as the Maremane Dome. This tilting and related uplift was followed by erosion of both the Asbestos Hills subgroup and the underlying Campbellrand Subgroup prior to the deposition of the Mapedi Formation of the Olifantshoek Supergroup (Figure 5.6.B). This erosion led to the development of a regional unconformity. During this period, both surficial and subsurface karstification processes began within the dolomites of the Campbellrand Subgroup. As described by Plehwe-Leisen and Klemm (1995), the karstification developed along zones of weakness caused by tectonic activity. Where banded iron-formation overlay the dolomites, cave systems developed. It was during this period of erosion that the Doornfontein conglomerates were deposited within the sinkholes. The residual contents of karstic sinkholes are not only a function of the composition of the formation being dissolved at the time but also of the composition of previously overlying dolomites that had already been dissolved.

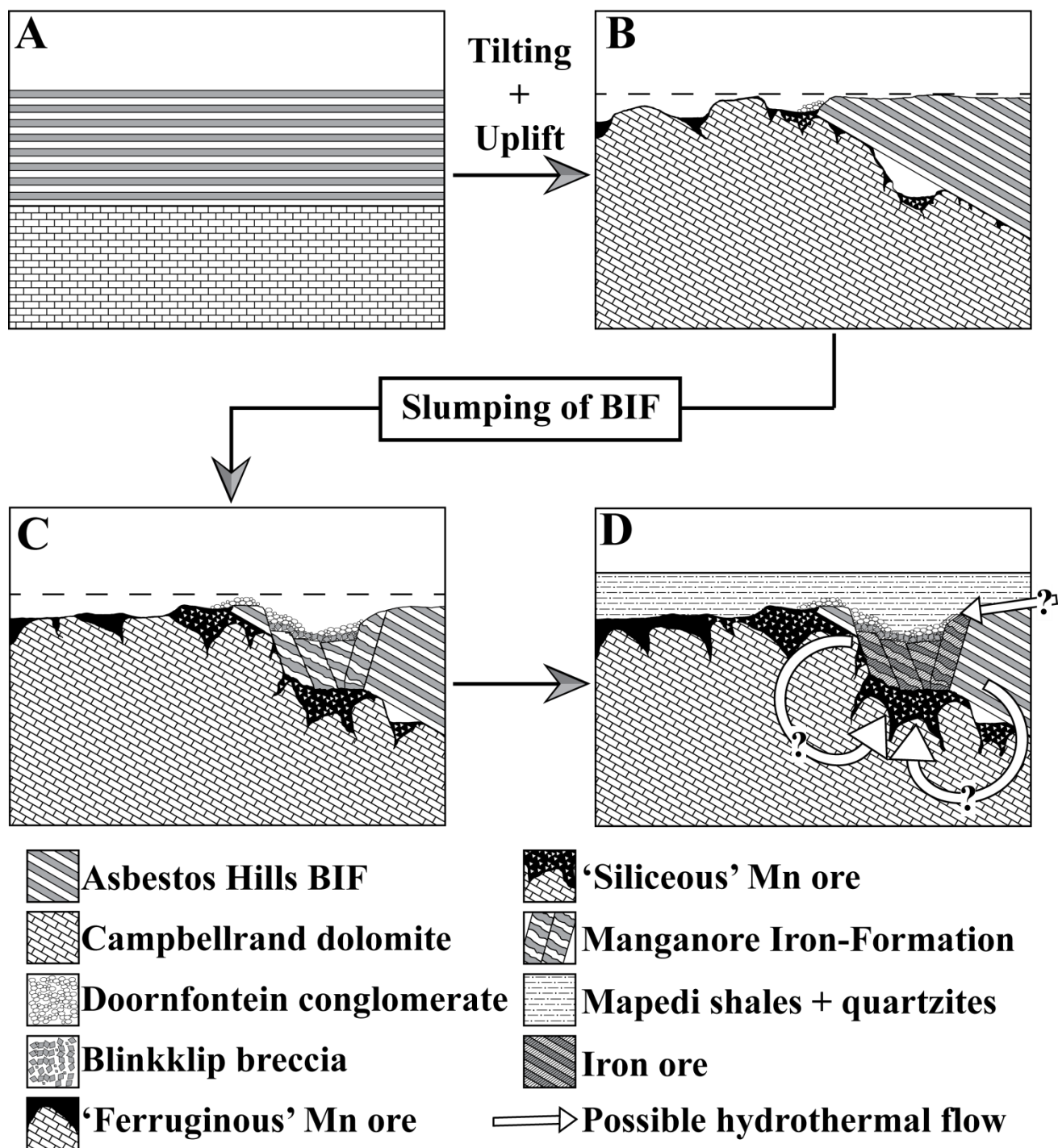


Figure 5.6: Model of ore formation for all ancient manganese deposits of the Postmasburg manganese field. **A.** Deposition of the Campbellrand and Asbestos Hills Subgroups. **B.** Tilting and uplift followed by erosion and dissolution of the Campbellrand dolomites. **C.** Continued dissolution and slumping of BIF into karstic sinkholes. Deposition of the Blinkklip breccia and Doornfontein conglomerate. **D.** Fluid influx, upgrading of BIF to Fe-ore and leaching of Na, Si, and K. Related metasomatism of manganese ores and deposition of alkali assemblages.

Continued dissolution caused the development of new sinkholes and an increase in size of existing sinkholes. The increased size of cave systems below the Asbestos Hills Subgroup caused the BIF to destabilize, collapse and slump into the underlying karstic depressions (Figure 5.6.C). It was during this process that the Blinkklip iron-formation breccia formed. The shales and quartzites of the Mapedi Formation were later deposited over the erosion surface. Dissolution continued during this phase of deposition and karstic depression continued to deepen, thus causing syn-depositional faulting and slumping in the Mapedi Formation (Figure 5.6.D).

At a later stage hydrothermal activity affected the Transvaal Supergroup stratigraphy. The timing of this hydrothermal event has not yet been fully constrained (as discussed in section 5.2 in this chapter) but it was likely to have occurred at or later than the Kheis orogenic event at around 1800 Ma (Moen, 2006). The hydrothermal event likely involved evolved, warm, oxidized, basinal brines that were enriched in alkalis and barium. These brines were responsible for alkali metasomatic alteration of the PMF ores and may have even contributed, in part, to the dissolution of Campbellrand dolomites. The source of the metals enriched in the hydrothermal fluid is still largely undetermined but a likely source of sodium and potassium is the banded iron-formations of the Transvaal Supergroup. The existence of anomalous abundances of authigenic riebeckite (Na-Fe amphibole) in the Hotazel Formation are documented by Fairey *et al.* (2013). The presence of riebeckite and stilpnomelane (K-Mg-Fe phyllosilicate) is also noted throughout most of the Asbestos Hills Subgroup by Beukes and Klein (1990).

Therefore the importance of the PMF ores is highlighted by at least a causal link between the hydrothermal alteration of the PMF ores and the upgrading of the iron ores of the Sishen type. That is, leaching of sodium and potassium and silicon from the overlying Asbestos Hills Subgroup and consequent upgrading of these banded iron-formation to iron ore by basinal brines may have provided the metals required for the alkali metasomatism that is evident in the PMF ores.

5.5. Concluding Remarks

The pigeon-hole-type classification of the Postmasburg manganese ores into Western and Eastern Belt or ferruginous and siliceous ores and the associated models require revision. The variability in chemical composition and stratigraphic setting of these deposits requires a more holistic approach to modelling their genesis. Furthermore, the manganese ore deposits of the Postmasburg Manganese

Field host complex mineral assemblages that must be accounted for when considering ore formation. Such gangue assemblages provide evidence for a single hydrothermal event that affected the rocks of the Transvaal Supergroup. On-going research of these assemblages is revealing a potential regional scale hydrothermal system that involved oxidized, alkaline brines. Such brines may have been responsible for the upgrading of various ore deposits in the region.

5.6. Future Research

A great deal of research is still required in the Postmasburg Manganese Field to further constrain hydrothermal processes occurring both on a local and regional scale in order to better understand processes of manganese- as well as iron-ore formation in the area. Experimental oxygen isotopic data for laboratory-synthesised braunite would provide an excellent base-line to study manganese ore forming processes not only in the PMF but in manganese deposits worldwide. This is due to the fact that braunite is usually a major component of manganese ores. More detailed work (e.g. Raman spectroscopy) on rare minerals such as arsenotokyoite and noélbensonite will help to characterize these phases. Additionally, fluid inclusion studies of various phases within the PMF ores would further constrain the depositional/crystallization histories of these phases. Finally, $^{40}\text{Ar}/^{39}\text{Ar}$ dating of microcline from this study may further constrain the age of hydrothermal activity.

Chapter 6

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Appendix I

List of Abbreviations

aeg	Aegirine
aug	Augite
ab	Albite
arm	Armbrusterite
atk	Arsenotokyoite
b.d	Below detection limit
ban	Banalsite
brt	Barite
br	Braunite
cal	Calcite
fsp	Feldspar
hem	Hematite
hol	Hollandite
KMF	Kalahari Manganese Field
LOI	Loss on ignition
mc	Microcline
n	Number of samples/analyses
n.c.	Not calculated
n.d.	Not determined
ntr	Natrolite
nl	Noélbensonite
ppm	Parts per million
pg	Paragonite
prt	Partridgeite
pim	Piemontite
PMF	Postmasburg Manganese Field
PPL	Plane-polarized light
qtz	Quartz
srd	Sérandite
str	Strontianite
sug	Sugilite
wt. %	Weight percent
with	Witherite
XPL	Cross-polarized light
XRD	X-Ray Diffraction

Appendix II

Core logs and sample depths

The two drill cores that were observed in detail are SLT-015 and SLT-017. A log of drill core SLT-018 has not been included due to the high amount of thrust faulting in most of the drill core which complicates the stratigraphy. Below is the graphical representation of samples in drill core SLT-015, SLT-017 and AKH-49 in Figure II-A, Figure II-B and Figure II-C respectively. Also included is Table II-A which contains depth information for all samples that were originally selected for use in this thesis.

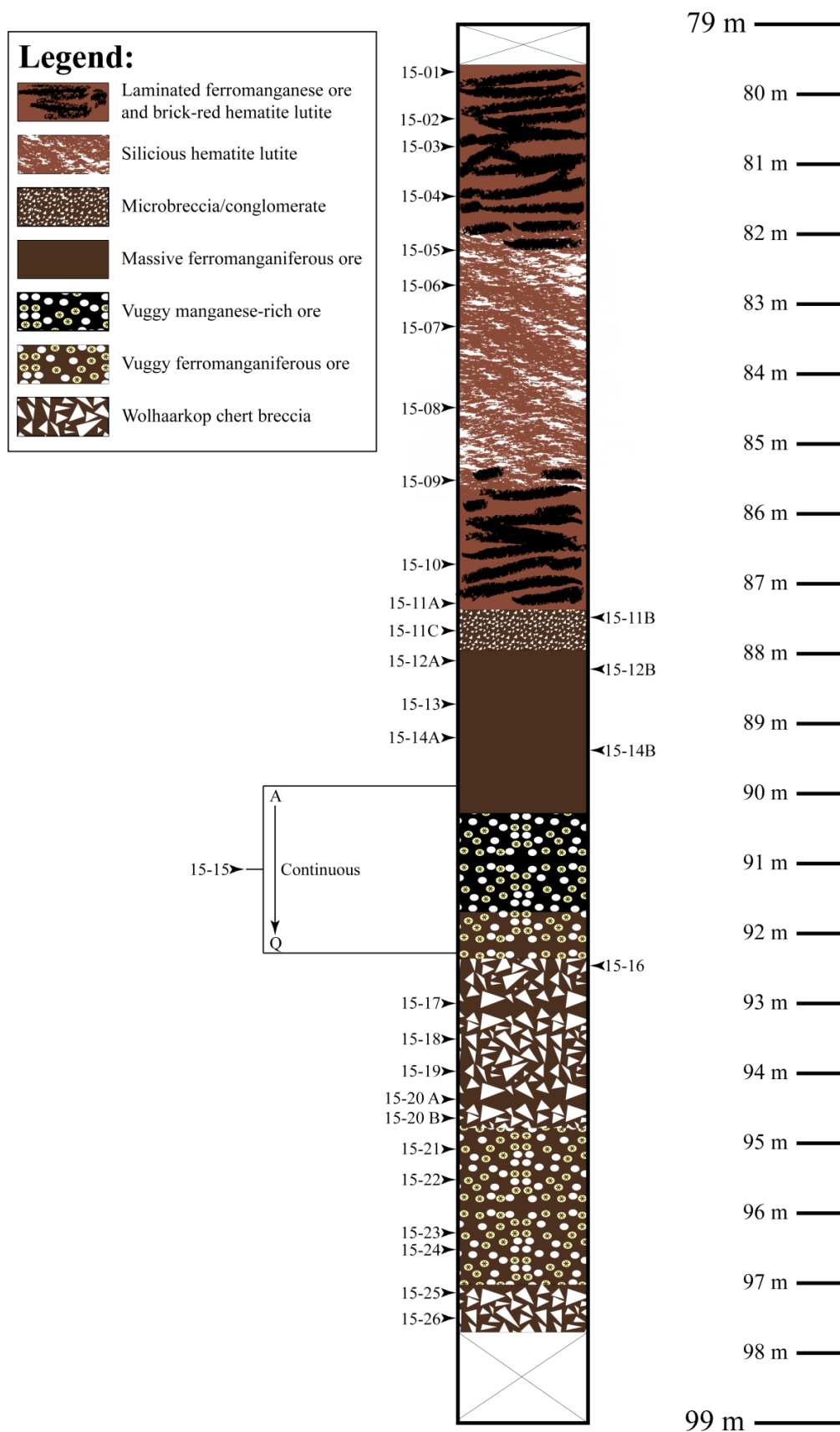


Figure II-A: Stratigraphic positions of samples in drill core SLT-015.

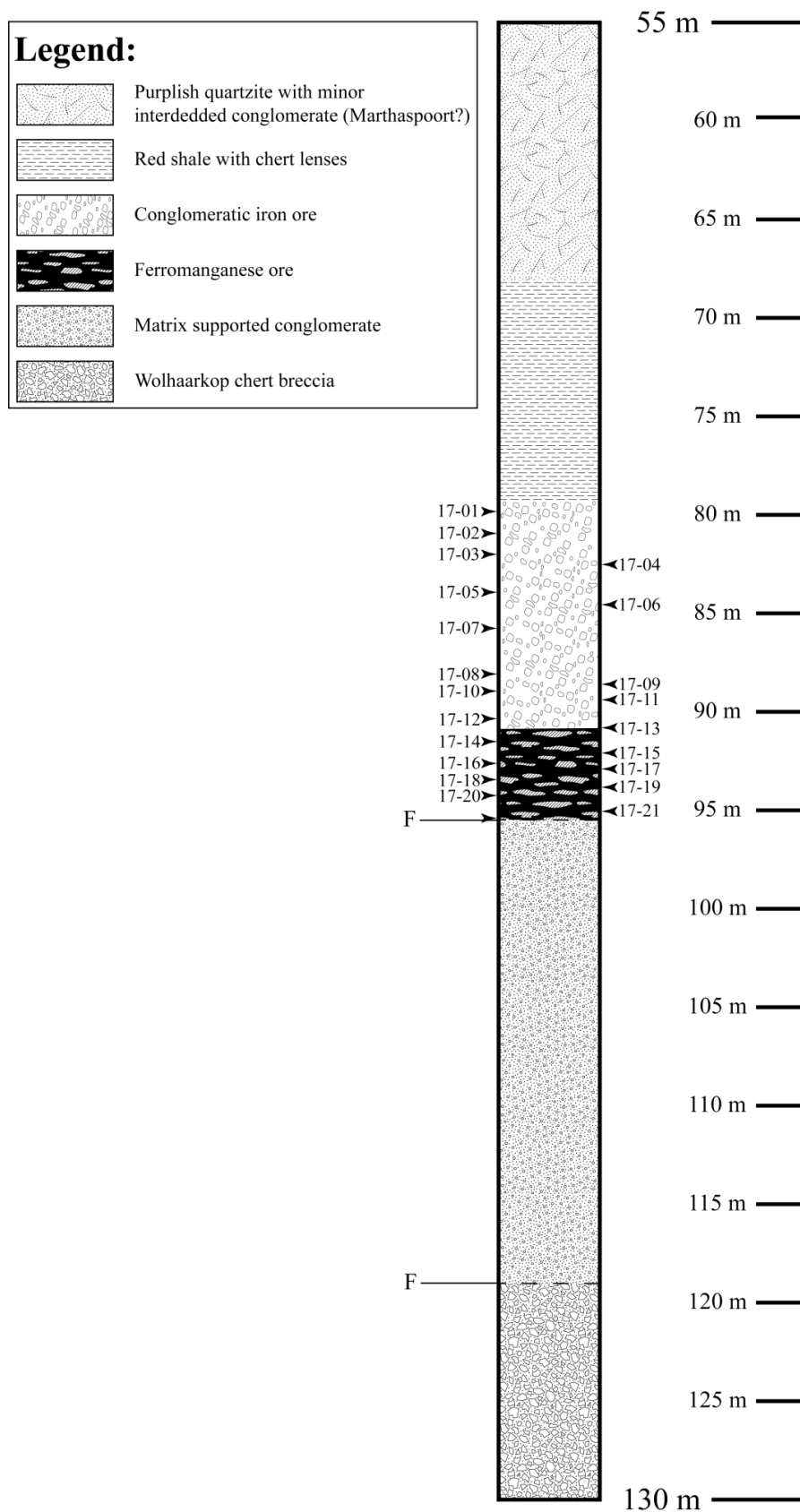


Figure II-B: Stratigraphic positions of samples in drill core SLT-017.

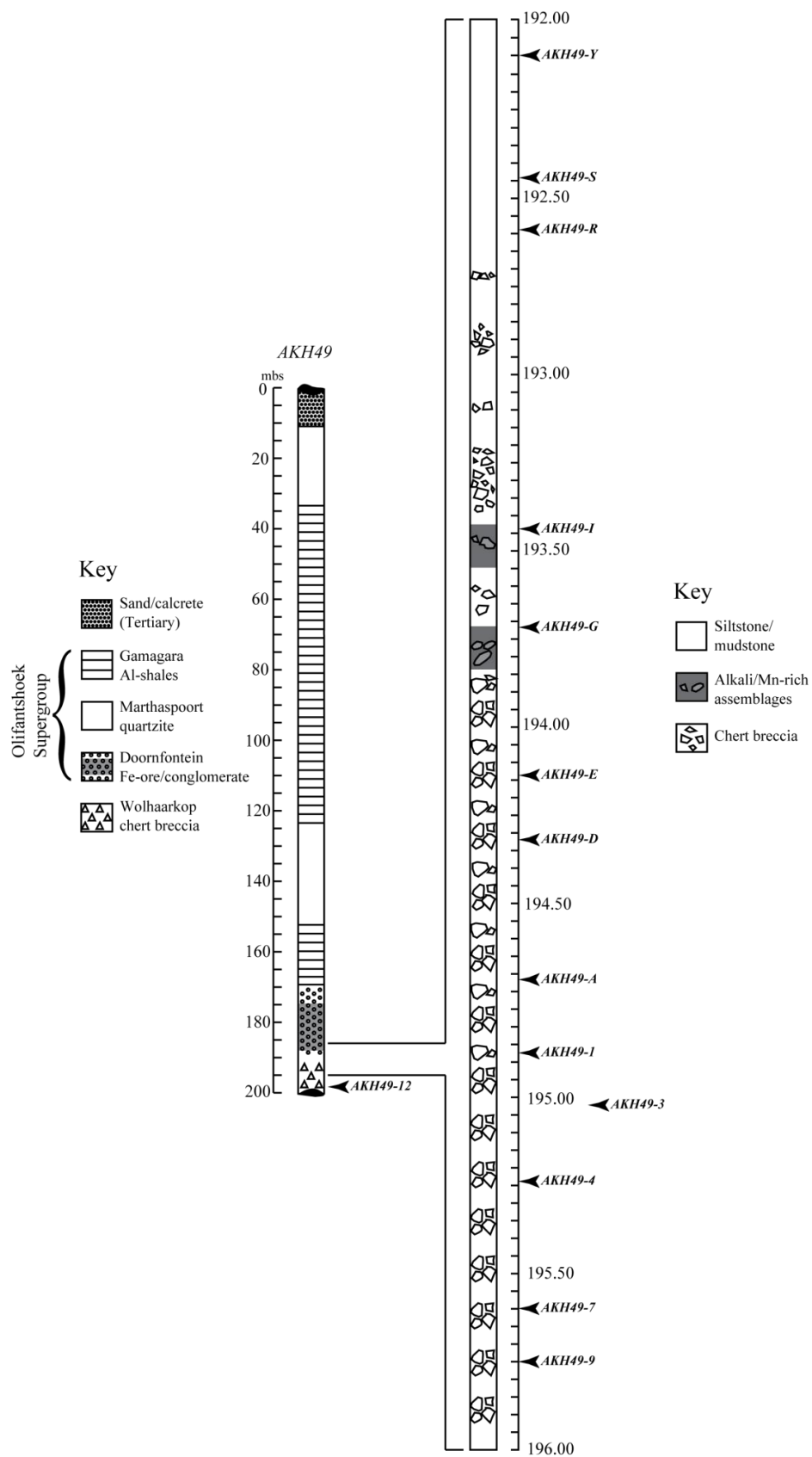


Figure II-C: Stratigraphic positions of samples in drill core AKH49 (modified after Moore *et al.*, 2011).

Table II-A: Samples depths for the drill cores used in this study.

SLT-015		SLT-017		SLT-018		AKH-49	
Sample Number	Depth (m)	Sample Number	Depth (m)	Sample Number	Depth (m)	Sample Number	Depth (m)
15-01	79.68	17-01	79.83	18-01	99.70	AKH49-Y	192.10
15-02	80.35	17-02	80.94	18-02	135.45	AKH49-S	192.44
15-03	80.75	17-03	82.00	18-03	136.90	AKH49-R	192.58
15-04	81.46	17-04	82.52	18-04	139.22	AKH49-I	193.44
15-05	82.23	17-05	83.93	18-05	141.22	AKH49-G	193.71
15-06	82.73	17-06	84.56	18-06	142.25	AKH49-E	194.13
15-07	83.32	17-07	85.76	18-07	142.82	AKH49-D	194.32
15-08	84.48	17-08	88.08	18-08	143.13	AKH49-A	194.71
15-09	85.52	17-09	88.60	18-09	143.34	AKH49-1	194.86
15-10	86.72	17-10	88.95	18-10	144.26	AKH49-3	195.08
15-11A	87.28	17-11	89.39	18-11	145.27	AKH49-4	195.24
15-11B	87.48	17-12	90.35	18-12	145.79	AKH49-7	195.60
15-11C	87.67	17-13	90.81	18-13	148.18	AKH49-9	195.75
15-12A	88.10	17-14	91.51	18-14	149.63	AKH49-12	ca. 198
15-12B	88.22	17-15	92.09	18-15	151.13		
15-13	88.72	17-16	92.62	18-16	151.83		
15-14A	89.21	17-17	92.90	18-17	152.93		
15-14B	89.38	17-18	93.44	18-18	154.35		
15-15 A-Q	89.89-92.28	17-19	93.83	18-19	157.11		
15-16	92.46	17-20	94.25				
15-17	93.00	17-21	95.05				
15-18	93.51	17-22	95.40				
15-19	93.97						
15-20A	94.37						
15-20B	94.64						
15-21	95.09						
15-22	95.52						
15-23	96.28						
15-24	96.52						
15-25	97.14						
15-26	97.50						

Appendix III

Analytical Techniques

i. Sample Preparation

Polished briquettes and polished thin sections were prepared at the Department of Geology at Rhodes University. Bulk rock powders, for XRD, XRF and ICP-MS were produced from samples composed of matrix only. This was done by selecting approximately 50 g of homogenous matrix from quartered drill core samples. These were then split into small pieces and crushed to a fine powder using a swing mill and a hardened steel set and rings at the Department of Geology, Rhodes University. This crushing equipment was thoroughly cleaned. First the equipment was scrubbed with detergent. The detergent was removed using tap water. The equipment was then wiped thoroughly with distilled water. Finally, acetone and pressurized air was used to dry the equipment. The sample was milled for 5 minutes to ensure that no coarse fraction remained. The rock powder was then stored in glass vials. In addition to the cleaning process, two batches of fresh quartzite were milled one after the other in order to reduce the possibility of any cross contamination between samples. Mineral separates of braunite were hand-picked under a binocular microscope after being coarse-crushed by hand. Once approximately 50 mg of braunite was selected it was crushed with an agate mortar and pestle to form a fine powder.

ii. X-Ray Diffraction (XRD)

The Bruker D8 Discover X-ray diffractometer, equipped with a Lynx Eye detector, was used to acquire bulk-rock powder XRD patterns. Approximately 1 g of powder was packed onto a plastic, indented plate. Cu-K_α radiation (= 1.5405 Å, nickel filter) was used and the X-ray diffraction data was treated using the Eva (evaluation curve fitting) software. Baseline correction was performed on each diffraction pattern.

iii. Determination of H_2O^- and loss on ignition (LOI)

The H_2O^- and LOI were determined at the Department of Geology, Rhodes University. Silica crucibles were used to hold the powdered samples. These crucibles were first cleaned with distilled water and left to dry in an oven at 110°C for 2 hours. They were then left to cool in a desiccator. The crucibles were then weighed to the fourth decimal place. Two grams of sample was placed in the crucibles and the mass of the sample and crucible were recorded to the fourth decimal. The sample was dried at 110°C for a minimum of 4 hours then placed in a desiccator to cool. The difference in mass between the sample and crucible before and after drying represents the H_2O^- of the sample. Following this, the same samples were ignited for a minimum of 6 hours at 900°C in a blast furnace. The samples were then left in a desiccator to cool. The difference in mass between the original sample and crucible and the mass after ignition represents the mass of adsorbed and structurally bound volatiles in the samples.

iv. X-Ray Fluorescence (XRF)

Major oxide compositions were determined at the Department of Geology, Rhodes University. The XRF techniques of Norrish and Hutton (1969) were used to make these determinations. Once the LOI had been determined as outlined earlier, 0.28 g of each ashed sample was fused with 0.02g NaNO_3 and 1.5 g lithium tetraborate flux to form glass disks. The K-alpha line for each major element was then used to analyse the disks. Background corrections were made based on “blank” materials. In the majority of the samples in this thesis, BaO occurs as one of the major oxides.

BaO, Na_2O and trace elements were measured by analysis of pressed powder briquettes. These briquettes are made using approximately 5g of powdered sample. The sample is mixed with an organic binding agent (Mowiol®) and cased in boric acid. It is then pressed using a hydraulic press. The trace elements that were determined are Zn, Cu, Ni, Co, Cr, V, Ba, Sc, Th, Pb, Y, Nb, Zr, Rb and Sr. In most samples, the barium concentrations were much higher than the available standard material. In such cases, the samples were diluted between 10 and 20 times using PURATRONIC ® silicon (IV) oxide. The barium concentrations were then back-calculated according to the relevant dilution factor. The sodium concentrations were also measured on diluted samples and the

difference in concentration between the original sodium values and the back-calculated values was used to normalize the back-calculated barium concentrations.

Trace and major element concentrations were determined using a Philips PW1410 XRF spectrometer in the Department of Geology, Rhodes University. The instrument was calibrated using international and in-house rock standards.

v. Electron Probe Microanalysis (EPMA)

Major element analyses were performed on various minerals using a Jeol JXA 8230 Superprobe with 4 WD spectrometers at the Department of Geology, Rhodes University. Polished thin sections and briquettes were first prepared for analysis by coating with carbon at a thickness of 20 nm. The analytical conditions for spot analyses as well as element maps were as follows:

- Acceleration voltage: 15 kV
- Probe current: 20 nA
- Counting time: 10 seconds on peak and 5 seconds on background
- ZAF matrix corrections

Qualitative WDS scans were first used to identify major elements in unknown minerals. The majority of quantitative analyses were performed using a spot beam size of less than 1 μm . However, matrix analyses were performed using a beam radius of 10 μm or 20 μm so as to include all extremely fine-grained phases and attain an approximately homogenous, bulk analysis of the matrix. A 10 μm beam radius was used for albite and natrolite analyses. Various standard materials were used depending upon the mineral analysed as shown in Table III-A and Table III-B below.

Table III-A: SPI© standard reference materials used for microprobe analyses of aegirine, albite, banalsite, barite, barytocalcite, braunite, dolomite, hematite and microcline.

	Aegirine	Albite	Banalsite	Barite	Barytocalcite	Braunite	Dolomite	Hematite	Microcline
Si	Olivine	Olivine	Diopside			Olivine		Olivine	Fayalite
Ti								Rutile	
Al	Almandine	Almandine	Almandine			Albite		Orthoclase	Albite
Fe	Fayalite	Almandine	Almandine	Hematite	Fayalite	Hematite	Almandine	Hematite	Fayalite
Mn	Rhodonite	Rhodonite	Rhodonite		Rhodonite	Rhodonite	Rhodonite	Spessartine	Rhodonite
V									
As									
Ba			Barite	Barite	Barite		Barite		Barite
Ca	Diopside	Cr-diopside	Cr-diopside	Diopside	Dolomite	Cr-diopside	Cr-diopside	Cr-diopside	Calcite
Mg	Diopside	Olivine	Diopside	Dolomite	Dolomite	Tremolite	Olivine	Periclase	
K	Orthoclase	Orthoclase	Orthoclase						Orthoclase
Na	Albite	Plag-An65	Jadeite						Albite
Cr								Cr ₂ O ₃	
S				Barite			Barite		
Sr				Celestite	Celestite	Celestite	SrTiO ₃		Celestite

Table III-B: SPI© standard reference materials used for microprobe analyses of natrolite, noélbensonite, paragonite, partridgeite, sérandite-pectolite group minerals, piemontite, arsenotokyoite and witherite.

	Natrolite	Noelbensonite	Paragonite	Partridgeite	Serandite-Pectolite	Piemontite	Arsenotokyoite	Witherite
Si	Olivine	Bustamite	Olivine	Olivine	Olivine	Olivine		
Ti			Rutile			Rutile		
Al	Almandine	Albite	Almandine	Albite	Albite	Kyanite		
Fe	Almandine			Hematite	Hematite	Almandine		Fayalite
Mn	Rhodonite	Bustamite	Rhodonite	Rhodonite	Rhodonite	Rhodonite	Rhodonite	Rhodonite
V							V metal	
As							Arsenopyrite	
Ba		Barite					Barite	Barite
Ca	Cr-diopside	Cr-diopside	Cr-diopside	Cr-diopside	Diopside	Cr-diopside		Dolomite
Mg	Olivine		Olivine	Tremolite	Tremolite	Olivine		Dolomite
K	Orthoclase		Orthoclase		Orthoclase	Orthoclase		
Na	Plag-An65		Albite		Albite	Albite		
Cr			Cr ₂ O ₃			Cr ₂ O ₃		
S								
Sr		Celestite						Celestite

vi. Stable isotope analysis

For oxygen isotopes, approximately 10 mg of braunite separate powder sample was reacted with ClF_3 . The liberated O_2 was converted to CO_2 using a hot platinized carbon rod. The data were measured using a gas-source Finnigan Delta XP mass spectrometer at the University of Cape Town. The measurements were conducted in offline, dual inlet mode. Further details, including standard materials, are outlined in Fourie and Harris (2011).

The same technique was applied for the measurement of carbon isotopic compositions of the dolomites. Bulk-rock dolostone samples were dissolved at 50°C and the data was recalculated assuming all the carbonate was dolomite.

Appendix IV

EPMA Data

This Appendix contains all the EPMA analyses which are represented by averages in the Chapter 3 of this thesis. The analyses for each mineral are tabulated separately. H₂O in hydrous phases has been calculated according to the mineral formula.

Abbreviations:

n.d: not determined.

Table IV-A: Electron microprobe data for aegirine in drill core SLT-015.

	Sample Number	Oxide (wt. %)								Cations calculated on the basis of 6O									
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	Na ₂ O	Total	Si	Al	Fe	Mn	Mg	Ca	K	Na	
A13	15-15N	52.46	1.00	30.05	1.31	0.04	0.09	0.02	14.08	99.03	2.02	0.05	0.87	0.04	0.00	0.00	0.00	1.05	
	15-15N	52.51	1.11	29.11	1.49	0.09	0.17	0.04	14.09	98.60	2.03	0.05	0.85	0.05	0.01	0.01	0.00	1.06	
	15-15N	52.01	0.27	31.65	0.92	0.03	0.04	<0.007	14.14	99.05	2.02	0.01	0.92	0.03	0.00	0.00	0.00	1.06	
	15-15N	52.76	0.75	29.94	1.11	0.95	0.77	0.03	13.67	99.97	2.02	0.03	0.86	0.04	0.05	0.03	0.00	1.01	
	15-15N	52.30	0.58	25.96	3.05	1.59	1.80	0.03	12.97	98.28	2.03	0.03	0.76	0.10	0.09	0.07	0.00	0.98	
	15-15N	52.44	0.25	31.42	0.63	<0.008	0.09	<0.008	13.88	98.71	2.03	0.01	0.92	0.02	0.00	0.00	0.00	1.04	
	15-15N	52.61	0.87	28.98	1.32	0.98	0.66	0.04	13.30	98.75	2.03	0.04	0.84	0.04	0.06	0.03	0.00	0.99	
	15-15N	51.94	0.23	32.13	0.36	0.03	0.03	0.04	14.00	98.76	2.02	0.01	0.94	0.01	0.00	0.00	0.00	1.05	
	15-15N	51.61	0.24	31.74	0.69	0.02	0.05	0.02	13.81	98.18	2.02	0.01	0.93	0.02	0.00	0.00	0.00	1.05	
	15-15N	52.03	0.23	31.54	0.86	0.02	0.02	0.04	13.86	98.58	2.02	0.01	0.92	0.03	0.00	0.00	0.00	1.04	
	15-15N	51.69	0.19	31.67	0.83	<0.01	0.02	0.03	13.86	98.29	2.02	0.01	0.93	0.03	0.00	0.00	0.00	1.05	
	15-15N	51.79	0.19	32.16	0.80	0.02	0.02	<0.007	14.15	99.12	2.01	0.01	0.94	0.03	0.00	0.00	0.00	1.06	
	15-15N	52.29	1.47	28.48	1.58	0.09	0.03	0.00	14.26	98.20	2.03	0.07	0.83	0.05	0.01	0.00	0.00	1.07	
	15-15N	52.04	0.22	31.84	0.82	0.02	0.01	<0.007	14.05	99.00	2.02	0.01	0.93	0.03	0.00	0.00	0.00	1.06	
	15-15O	52.34	0.27	31.62	0.63	0.04	0.12	0.17	14.42	99.66	2.02	0.01	0.92	0.02	0.00	0.01	0.01	1.08	
	15-15O	52.12	0.28	31.29	0.45	0.01	0.11	0.16	14.48	98.89	2.02	0.01	0.91	0.01	0.00	0.00	0.01	1.09	
	15-15O	52.75	0.71	29.94	0.88	0.87	0.84	0.03	13.61	99.63	2.02	0.03	0.86	0.03	0.05	0.03	0.00	1.01	
	15-15I	52.52	0.87	29.45	1.08	0.19	0.23	0.04	14.20	98.56	2.03	0.04	0.86	0.04	0.01	0.01	0.00	1.07	
	15-15I	52.40	0.33	31.23	1.02	0.05	0.16	0.02	14.64	99.84	2.02	0.01	0.90	0.03	0.00	0.01	0.00	1.09	
		Average	52.24	0.53	30.54	1.04	0.30	0.28	0.05	13.97	98.90	2.02	0.02	0.89	0.03	0.02	0.01	0.00	1.05
		Std. Dev.	0.34	0.38	1.61	0.59	0.48	0.45	0.05	0.40	0.55								
		Minimum	51.61	0.19	25.96	0.36	<0.008	0.01	<0.007	12.97	98.18								
		Maximum	52.76	1.47	32.16	3.05	1.59	1.80	0.17	14.64	99.97								

Table IV-B: Electron microprobe data for albite in drill core SLT-015.

	Sample Number	Oxide (wt. %)								Cations calculated on the basis of 8 O								
		SiO ₂	Al ₂ O ₃	FeO	MnO	K ₂ O	MgO	CaO	Na ₂ O	Total	Si	Al	Fe	Mn	K	Mg	Ca	Na
A14	15-15E	69.76	19.26	<0.043	<0.014	<0.005	<0.007	0.01	12.01	101.03	3.01	0.98	0.00	0.00	0.00	0.00	0.00	1.01
	15-15E	69.30	19.32	<0.049	<0.014	0.02	<0.006	0.01	11.81	100.46	3.01	0.99	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	68.96	19.45	<0.044	0.03	0.01	<0.006	0.01	11.90	100.35	3.00	1.00	0.00	0.00	0.00	0.00	0.00	1.00
	15-15E	69.62	19.39	<0.039	<0.014	0.03	0.01	0.01	11.70	100.77	3.01	0.99	0.00	0.00	0.00	0.00	0.00	0.98
	15-15E	68.99	19.51	<0.043	<0.013	0.01	<0.006	0.01	11.74	100.27	3.00	1.00	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	69.21	19.37	<0.042	0.02	0.02	<0.006	0.02	11.88	100.51	3.01	0.99	0.00	0.00	0.00	0.00	0.00	1.00
	15-15E	69.14	19.37	0.09	0.04	0.01	<0.006	0.01	11.70	100.37	3.01	0.99	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	69.09	19.55	<0.042	<0.013	0.01	<0.006	0.03	11.69	100.38	3.00	1.00	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	68.34	19.17	0.05	<0.013	0.02	<0.007	0.03	11.26	98.87	3.01	1.00	0.00	0.00	0.00	0.00	0.00	0.96
	15-15E	68.38	19.39	<0.043	0.03	0.02	<0.006	0.02	11.42	99.25	3.00	1.00	0.00	0.00	0.00	0.00	0.00	0.97
	15-15E	68.77	19.40	<0.043	<0.013	0.01	<0.006	0.02	11.76	99.97	3.00	1.00	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	69.19	19.15	<0.042	<0.014	<0.005	<0.006	0.04	11.85	100.23	3.01	0.98	0.00	0.00	0.00	0.00	0.00	1.00
	15-15E	69.14	19.22	<0.043	0.02	0.02	<0.006	0.02	11.82	100.24	3.01	0.99	0.00	0.00	0.00	0.00	0.00	1.00
	15-15E	68.19	19.16	<0.041	0.07	0.02	<0.006	0.02	11.56	99.01	3.00	1.00	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	68.84	19.30	<0.041	<0.014	0.02	<0.006	0.02	11.74	99.91	3.01	0.99	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	68.44	19.09	0.07	0.03	0.01	<0.006	0.01	11.61	99.26	3.01	0.99	0.00	0.00	0.00	0.00	0.00	0.99
	15-15E	68.69	19.25	<0.039	<0.015	0.02	<0.006	0.01	11.77	99.75	3.01	0.99	0.00	0.00	0.00	0.00	0.00	1.00
	Average	68.94	19.31	0.07	0.03	0.02		0.02	11.72	100.04	3.01	0.99	0.00	0.00	0.00	0.00	0.00	0.99
	Std. Dev.	0.44	0.13	0.02	0.02	0.01		0.01	0.18	0.62								
	Minimum	68.19	19.09	<0.039	<0.013	<0.005	<0.006	0.01	11.26	98.87								
	Maximum	69.76	19.55	0.09	0.07	0.03	0.01	0.04	12.01	101.03								

Table III-C: Electron microprobe data for barite in drill core SLT-015.

	Sample Number	Oxide (wt. %)							Cations calculated on the basis of 4O					
		CaO	MgO	FeO	BaO	SO ₃	SrO	Total	Ca	Mg	Fe	Ba	S	Sr
	15-11B	<0.011	<0.007	0.11	65.63	33.88	0.03	99.64	0.00	0.00	0.00	1.01	1.00	0.00
	15-11B	0.03	0.02	<0.034	65.84	33.98	0.01	99.88	0.00	0.00	0.00	1.01	1.00	0.00
	15-11B	<0.012	<0.007	<0.037	65.24	34.33	<0.01	99.57	0.00	0.00	0.00	0.99	1.00	0.00
	15-11B	0.07	0.02	<0.036	65.72	33.80	0.01	99.61	0.00	0.00	0.00	1.01	1.00	0.00
	15-11B	0.06	<0.007	<0.036	65.49	34.06	<0.01	99.61	0.00	0.00	0.00	1.00	1.00	0.00
	15-11B	0.03	<0.007	0.02	65.03	34.18	0.01	99.27	0.00	0.00	0.00	0.99	1.00	0.00
	15-11B	0.04	0.01	0.17	64.82	34.44	<0.01	99.47	0.00	0.00	0.01	0.99	1.00	0.00
	Average	0.05	0.01	0.10	65.39	34.10	0.01	99.58	0.00	0.00	0.00	1.00	1.00	0.00
Std. Dev.	0.02	0.01	0.08	0.38	0.23	0.01	0.18							
Minimum	<0.011	<0.007	0.02	64.82	33.80	<0.01	99.27							
Maximum	0.07	0.02	0.17	65.84	34.44	0.03	99.88							

Table IV-D: Electron microprobe data for braunite in drill core SLT-015.*MnO calculated according to braunite formula.

	Sample Number	Oxide (wt. %)								Cations calculated on the basis of 12O									
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	MgO	CaO	SrO	MnO	Total	Si	Al	Fe	Mn ³⁺	Mn ²⁺	Mg	Ca	Sr	
A16	15-06	10.01	0.38	1.99	75.81	0.09	1.50	<0.008	9.80	99.57	1.01	0.04	0.15	5.79	0.83	0.01	0.16	0.00	
	15-06	9.78	1.16	5.66	70.45	0.02	0.85	<0.008	10.50	98.42	0.99	0.14	0.43	5.44	0.90	0.00	0.09	0.00	
	15-06	9.67	0.17	0.64	77.39	0.05	0.72	<0.008	10.40	99.05	0.98	0.02	0.05	5.97	0.89	0.01	0.08	0.00	
	15-06	9.85	0.46	0.37	76.35	0.06	1.08	0.02	10.00	98.19	1.00	0.05	0.03	5.92	0.86	0.01	0.12	0.00	
	15-06	10.14	0.49	0.71	77.66	0.02	1.66	<0.007	9.80	100.48	1.01	0.06	0.05	5.88	0.83	0.00	0.18	0.00	
	15-06	9.76	0.19	0.16	78.29	0.08	0.85	<0.008	10.30	99.62	0.98	0.02	0.01	6.00	0.88	0.01	0.09	0.00	
	15-06	9.75	1.70	0.28	75.39	<0.006	1.61	0.01	9.40	98.14	0.99	0.20	0.02	5.81	0.81	0.00	0.17	0.00	
	15-06	9.35	0.71	0.52	79.10	0.01	0.46	<0.007	10.50	100.64	0.93	0.08	0.04	6.01	0.89	0.00	0.05	0.00	
	15-06	9.53	0.54	0.18	77.73	<0.006	1.71	<0.007	9.10	98.79	0.96	0.06	0.01	5.99	0.78	0.00	0.19	0.00	
	15-06	9.77	0.72	4.20	73.85	0.06	1.42	<0.007	9.60	99.63	0.98	0.08	0.32	5.64	0.82	0.01	0.15	0.00	
	15-15A	9.92	1.08	3.19	73.67	0.15	1.79	<0.007	9.20	99.01	1.00	0.13	0.24	5.64	0.78	0.02	0.19	0.00	
	15-15A	9.86	1.15	3.93	72.83	0.12	1.79	<0.008	9.20	98.87	0.99	0.14	0.30	5.58	0.78	0.02	0.19	0.00	
	15-15A	10.01	1.27	3.92	72.19	0.17	1.82	0.03	9.20	98.61	1.01	0.15	0.30	5.54	0.78	0.02	0.20	0.00	
	15-15A	7.72	1.18	2.99	77.80	0.09	1.16	<0.007	7.50	98.43	0.79	0.14	0.23	6.05	0.65	0.01	0.13	0.00	
	15-15A	10.15	1.16	4.80	71.17	0.12	1.83	0.05	9.40	98.68	1.02	0.14	0.36	5.46	0.80	0.02	0.20	0.00	
	15-15A	9.28	1.03	2.76	75.78	0.10	1.44	0.07	8.90	99.35	0.93	0.12	0.21	5.80	0.76	0.01	0.16	0.00	
	15-15A	8.24	0.60	3.09	77.64	0.06	1.58	<0.007	7.60	98.81	0.84	0.07	0.24	6.02	0.66	0.01	0.17	0.00	
	15-15A	8.32	0.65	2.92	79.42	0.09	1.49	<0.007	7.80	100.69	0.83	0.08	0.22	6.04	0.66	0.01	0.16	0.00	
	15-15A	8.97	0.80	4.63	75.19	0.08	1.82	0.03	8.10	99.62	0.90	0.10	0.35	5.75	0.69	0.01	0.20	0.00	
	15-15E	10.50	0.35	4.70	71.48	0.12	1.92	0.06	9.70	98.84	1.06	0.04	0.36	5.49	0.83	0.02	0.21	0.00	
	15-15E	10.65	0.34	4.63	70.54	0.09	1.94	0.02	9.90	98.11	1.08	0.04	0.35	5.45	0.85	0.01	0.21	0.00	
	15-15E	10.66	0.42	4.62	71.83	0.08	2.04	<0.008	9.90	99.54	1.07	0.05	0.35	5.47	0.84	0.01	0.22	0.00	
	15-15E	10.68	0.42	4.67	71.42	0.12	1.99	0.03	9.90	99.23	1.07	0.05	0.35	5.45	0.84	0.02	0.21	0.00	
	15-15E	9.87	0.43	3.94	73.58	0.10	1.66	<0.007	9.40	98.97	1.00	0.05	0.30	5.66	0.80	0.02	0.18	0.00	
	15-15E	9.82	0.46	4.88	73.68	0.11	1.70	<0.007	9.30	99.94	0.98	0.05	0.37	5.61	0.79	0.02	0.18	0.00	
		Average	9.69	0.71	2.97	74.81	0.09	1.51	0.04	9.38	99.17	0.98	0.08	0.23	5.74	0.80	0.01	0.16	0.00
		Std. Dev.	0.74	0.40	1.82	2.85	0.04	0.43	0.02	0.85	0.74								
		Minimum	7.72	0.17	0.16	70.45	<0.006	0.46	<0.007	7.50	98.11								
		Maximum	10.68	1.70	5.66	79.42	0.17	2.04	0.07	10.50	100.69								

Table IV-E: Electron microprobe data for hematite in drill core SLT-015.

	Sample Number	Oxide (wt. %)						Cations calculated on the basis of 3O						
		TiO ₂	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	Mn ₂ O ₃	Cr ₂ O ₃	Total	Ti	Al	Si	Fe	Mn	Cr
A17	15-23B	<0.016	0.06	n.d	95.16	2.92	<0.011	98.14	0.00	0.00	0.00	1.94	0.06	0.00
	15-23B	<0.017	0.05	n.d	95.28	2.86	0.04	98.23	0.00	0.00	0.00	1.94	0.06	0.00
	15-23B	0.10	0.02	n.d	97.27	2.73	<0.011	100.12	0.00	0.00	0.00	1.94	0.06	0.00
	15-23B	0.10	0.07	n.d	93.65	6.25	0.02	100.08	0.00	0.00	0.00	1.87	0.13	0.00
	15-15E	0.21	0.16	n.d	96.48	3.65	<0.010	100.50	0.00	0.01	0.00	1.92	0.07	0.00
	15-15A	n.d	0.58	0.74	92.63	5.96	n.d	99.90	0.00	0.02	0.02	1.84	0.12	0.00
	15-15A	n.d	0.57	0.59	91.66	5.57	n.d	98.39	0.00	0.02	0.02	1.85	0.11	0.00
	15-15A	n.d	0.58	0.65	93.73	5.54	n.d	100.50	0.00	0.02	0.02	1.85	0.11	0.00
	15-15A	n.d	0.53	0.52	94.19	5.40	n.d	100.64	0.00	0.02	0.01	1.86	0.11	0.00
	15-15A	n.d	0.53	0.61	92.07	5.26	n.d	98.47	0.00	0.02	0.02	1.85	0.11	0.00
	15-23A	n.d	0.15	0.43	90.35	6.86	n.d	98.35	0.00	0.00	0.01	1.84	0.14	0.00
	15-14A	0.12	1.72	0.48	96.69	0.99	0.03	100.02	0.00	0.05	0.01	1.91	0.02	0.00
	15-14A	0.10	1.54	0.58	96.69	0.12	<0.020	99.03	0.00	0.05	0.02	1.93	0.00	0.00
	Average	0.12	0.50	0.57	94.30	4.16	0.03	99.41	0.00	0.02	0.01	1.89	0.08	0.00
	Std. Dev.	0.05	0.55	0.10	2.19	2.11	0.01	0.98						
	Minimum	<0.016	0.02	0.43	90.35	0.12	<0.010	98.14						
	Maximum	0.21	1.72	0.74	97.27	6.86	0.04	100.64						

Table IV-F: Electron microprobe data for microcline in drill core SLT-015.

[illegible]

Table IV-G: Electron microprobe data for natrolite in drill core SLT-015.

	Sample Number	Oxide (wt. %)								Cations calculated on the basis of 100								
		SiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	K ₂ O	Na ₂ O	Total	Si	Al	Fe	Mn	Mg	Ca	K	Na
A19	15-15E	47.85	26.12	0.15	0.24	<0.006	0.02	0.02	16.22	90.61	3.03	1.95	0.01	0.01	0.00	0.00	0.00	1.99
	15-15E	47.41	26.12	<0.046	0.58	<0.006	0.05	0.03	16.14	90.32	3.02	1.96	0.00	0.03	0.00	0.00	0.00	1.99
	15-15E	46.58	26.16	<0.039	<0.013	<0.006	0.01	0.03	16.27	89.07	3.00	1.99	0.00	0.00	0.00	0.00	0.00	2.03
	15-15E	46.23	26.09	<0.040	0.01	<0.006	0.02	0.02	15.78	88.15	3.00	2.00	0.00	0.00	0.00	0.00	0.00	1.99
	15-15E	46.30	26.02	<0.040	<0.013	<0.006	<0.005	0.01	16.03	88.36	3.00	1.99	0.00	0.00	0.00	0.00	0.00	2.02
	15-15E	47.11	26.45	0.03	0.04	<0.006	0.01	0.03	16.26	89.93	3.00	1.99	0.00	0.00	0.00	0.00	0.00	2.01
	15-15E	47.40	26.20	<0.039	0.04	<0.006	<0.005	0.02	16.27	89.93	3.02	1.97	0.00	0.00	0.00	0.00	0.00	2.01
	15-15E	47.61	26.39	<0.042	0.02	0.01	0.01	0.07	15.87	89.98	3.03	1.98	0.00	0.00	0.00	0.00	0.01	1.96
	15-15E	46.92	26.07	0.03	0.02	<0.006	0.02	0.04	16.07	89.16	3.02	1.97	0.00	0.00	0.00	0.00	0.00	2.00
	15-15E	46.77	26.11	0.05	0.06	<0.006	0.02	0.02	15.64	88.68	3.02	1.99	0.00	0.00	0.00	0.00	0.00	1.96
	15-15E	46.94	26.42	0.06	0.01	0.01	0.03	0.05	16.01	89.53	3.00	1.99	0.00	0.00	0.00	0.00	0.00	1.99
	Average	47.01	26.20	0.03	0.09	0.00	0.02	0.03	16.05	89.43	3.01	1.98	0.00	0.00	0.00	0.00	0.00	1.99
	Std. Dev.	0.52	0.15	0.05	0.18	0.00	0.01	0.02	0.21	0.81								
	Minimum	46.23	26.02	<0.039	<0.010	<0.006	<0.005	0.01	15.64	88.15								
Maximum	47.85	26.45	0.15	0.58	0.01	0.05	0.07	16.27	90.61									

Table IV-H: Electron microprobe data for noélbensonite in drill core SLT-015.

	Sample Number	Oxide (wt. %)							Cations calculated on the basis of 8O						
		SiO ₂	Al ₂ O ₃	Mn ₂ O ₃	BaO	CaO	SrO	H ₂ O	Total	Si	Al	Mn	Ba	Ca	Sr
A20	15-15O	27.63	0.23	36.28	24.09	1.89	1.79	8.22	100.12	2.02	0.02	2.02	0.69	0.15	0.08
	15-15O	27.43	0.19	35.29	25.25	1.12	2.61	8.10	99.99	2.03	0.02	1.99	0.73	0.09	0.11
	15-15O	27.19	0.22	35.39	27.39	1.00	1.56	8.09	100.85	2.02	0.02	2.00	0.80	0.08	0.07
	15-15O	27.32	0.23	35.22	26.56	0.81	2.23	8.08	100.46	2.03	0.02	1.99	0.77	0.06	0.10
	15-15O	27.62	0.20	34.20	26.42	2.01	1.44	8.09	99.97	2.05	0.02	1.93	0.77	0.16	0.06
	15-15O	28.32	0.22	34.76	25.36	2.25	1.79	8.25	100.94	2.06	0.02	1.92	0.72	0.17	0.08
	15-15O	28.20	0.16	35.15	25.44	1.63	1.53	8.20	100.30	2.06	0.01	1.96	0.73	0.13	0.06
	15-15O	27.37	0.21	35.71	24.90	1.22	1.70	8.09	99.20	2.03	0.02	2.01	0.72	0.10	0.07
	15-23A	26.06	0.28	34.78	29.88	0.38	1.36	7.89	100.62	1.98	0.03	2.01	0.89	0.03	0.06
	15-23A	27.63	0.20	37.35	23.62	0.66	2.80	8.23	100.49	2.01	0.02	2.07	0.67	0.05	0.12
	15-23B	27.55	0.22	34.42	26.83	0.85	2.63	8.07	100.57	2.05	0.02	1.95	0.78	0.07	0.11
	15-23B	28.02	0.22	34.01	26.62	0.71	2.84	8.10	100.51	2.07	0.02	1.92	0.77	0.06	0.12
	Average	27.53	0.22	35.21	26.03	1.21	2.02	8.12	100.33	2.03	0.02	1.98	0.75	0.10	0.09
	Std. Dev.	0.58	0.03	0.93	1.66	0.60	0.56	0.10	0.47						
	Minimum	26.06	0.16	34.01	23.62	0.38	1.36	7.89	99.20						
	Maximum	28.32	0.28	37.35	29.88	2.25	2.84	8.25	100.94						

Table IV-I: Electron microprobe data for paragonite in drill core SLT-015.

Sample number	Oxide (wt. %)											Cations calculated on the basis of 11O										
	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	K ₂ O	Na ₂ O	Cr ₂ O ₃	Total	Si	Ti	Al	Fe	Mn	Mg	Ca	K	Na	Cr	
15-09	49.11	<0.007	37.30	0.41	0.04	0.03	0.02	0.51	5.35	<0.01	92.77	3.18	0.00	2.84	0.02	0.00	0.00	0.00	0.04	0.67	0.00	
15-09	48.82	<0.007	37.46	0.37	0.04	0.01	0.05	0.38	5.21	<0.01	92.33	3.17	0.00	2.86	0.02	0.00	0.00	0.00	0.03	0.66	0.00	
15-09	49.11	<0.007	37.55	0.44	0.06	0.04	0.03	0.42	5.53	0.02	93.19	3.16	0.00	2.85	0.02	0.00	0.00	0.00	0.03	0.69	0.00	
15-09	47.97	0.01	37.84	1.36	0.10	0.03	0.04	0.51	5.24	0.03	93.12	3.11	0.00	2.89	0.07	0.01	0.00	0.00	0.04	0.66	0.00	
15-09	48.95	<0.007	37.63	0.53	0.06	0.05	0.01	0.39	5.07	0.03	92.72	3.16	0.00	2.87	0.03	0.00	0.00	0.00	0.03	0.64	0.00	
15-09	48.63	<0.007	37.45	0.25	0.07	0.02	0.02	0.43	5.46	0.04	92.36	3.16	0.00	2.87	0.01	0.00	0.00	0.00	0.04	0.69	0.00	
Average	48.76		37.54	0.56	0.06	0.03	0.03	0.44	5.31	0.03	92.75	3.16	0.00	2.86	0.03	0.00	0.00	0.00	0.04	0.67	0.00	
Std. Dev.	0.43		0.18	0.40	0.02	0.01	0.01	0.06	0.17	0.01	0.36											
Minimum	47.97	<0.007	37.30	0.25	0.04	0.01	0.01	0.38	5.07	<0.01	92.33											
Maximum	49.11	0.01	37.84	1.36	0.10	0.05	0.05	0.51	5.53	0.04	93.19											

Table IV-J: Electron microprobe data for partridgeite in drill core SLT-015.

Sample Number	Oxide (wt. %)							Cations calculated on the basis of 3O					
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	CaO	MgO	Total	Si	Al	Fe	Mn	Ca	Mg
15-15E	2.27	0.86	2.64	95.18	0.31	0.07	101.32	0.06	0.03	0.05	1.84	0.01	0.00
15-15E	2.28	0.62	3.34	96.11	0.28	0.05	102.68	0.06	0.02	0.06	1.84	0.01	0.00
15-15E	3.22	0.69	2.90	94.89	0.47	0.06	102.24	0.08	0.02	0.05	1.81	0.01	0.00
15-15E	1.47	0.64	3.07	97.00	0.19	0.03	102.40	0.04	0.02	0.06	1.87	0.01	0.00
15-15E	2.16	0.67	2.46	95.01	0.29	0.04	100.62	0.06	0.02	0.05	1.85	0.01	0.00
15-15E	2.11	0.47	3.67	95.24	0.31	0.04	101.85	0.05	0.01	0.07	1.84	0.01	0.00
Average	2.25	0.66	3.01	95.57	0.31	0.05	101.85	0.06	0.02	0.06	1.84	0.01	0.00
Std. Dev.	0.56	0.13	0.45	0.82	0.09	0.01	0.77						
Minimum	1.47	0.47	2.46	94.89	0.19	0.03	100.62						
Maximum	3.22	0.86	3.67	97.00	0.47	0.07	102.68						

Table IV-K: Electron microprobe data for piemontite in drill core SLT-015.

Sample Number	Oxide (wt. %)											Cations calculated on the basis of 12.5O									
	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Mn ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	H ₂ O	Total	Si	Ti	Al	Fe	Mn	Ca	Mg	K	Na	
15-11Cii	38.88	0.08	22.38	1.07	14.67	21.41	0.02	0.08	0.29	1.90	100.77	3.06	0.00	2.08	0.06	0.88	1.81	0.00	0.01	0.04	
15-11Cii	38.33	0.06	22.16	1.23	14.88	21.31	0.01	0.04	0.27	1.89	100.17	3.04	0.00	2.07	0.07	0.90	1.81	0.00	0.00	0.04	
15-11Cii	38.50	0.06	21.56	1.20	15.51	21.83	0.04	0.04	0.12	1.89	100.75	3.05	0.00	2.01	0.07	0.93	1.85	0.00	0.00	0.02	
Average	38.57	0.06	22.03	1.17	15.02	21.52	0.02	0.05	0.23	1.89	100.56	3.05	0.00	2.05	0.07	0.90	1.82	0.00	0.01	0.03	
Std. Dev.	0.28	0.01	0.42	0.08	0.44	0.27	0.02	0.02	0.09	0.01	0.34										
Minimum	38.33	0.06	21.56	1.07	14.67	21.31	0.01	0.04	0.12	1.89	100.17										
Maximum	38.88	0.08	22.38	1.23	15.51	21.83	0.04	0.08	0.29	1.90	100.77										

Table IV-L: Electron microprobe data for sérandite-pectolite group minerals in drill core SLT-015.

Sample number	Oxide (wt. %)										Cations calculated on the basis of 8.5 O									Per formula unit	
	SiO ₂	Al ₂ O ₃	FeO	MnO	MgO	K ₂ O	CaO	Na ₂ O	H ₂ O	Total	Si	Al	Fe	Mn	Mg	K	Ca	Na		Ca	Mn
15-15O	50.24	0.03	<0.03	35.21	0.03	0.01	2.67	8.87	2.50	99.55	3.01	0.00	0.00	1.79	0.00	0.00	0.17	1.03		0.07	0.93
15-15O	49.99	<0.008	<0.03	37.60	<0.005	<0.005	1.18	9.03	2.50	100.30	3.00	0.00	0.00	1.91	0.00	0.00	0.08	1.05		0.03	0.97
15-15O	49.71	0.02	<0.03	35.81	<0.005	0.01	2.23	9.19	2.49	99.46	2.99	0.00	0.00	1.83	0.00	0.00	0.14	1.07		0.06	0.94
15-15I	51.20	0.01	0.25	22.05	0.03	<0.006	14.84	9.39	2.58	100.34	2.97	0.00	0.01	1.08	0.00	0.00	0.92	1.06		0.40	0.60
15-15I	50.46	<0.008	0.12	31.39	0.03	0.03	6.03	8.63	2.51	99.19	3.01	0.00	0.01	1.59	0.00	0.00	0.39	1.00		0.16	0.84
15-15I	50.58	0.03	0.10	29.55	<0.005	0.03	7.65	8.55	2.52	99.01	3.01	0.00	0.01	1.49	0.00	0.00	0.49	0.99		0.21	0.79
15-15I	51.04	0.02	0.14	25.27	0.03	0.01	11.72	9.02	2.56	99.81	2.99	0.00	0.01	1.25	0.00	0.00	0.74	1.02		0.32	0.68
15-15I	50.78	<0.008	0.07	36.88	<0.005	0.03	1.88	8.62	2.53	100.79	3.01	0.00	0.00	1.85	0.00	0.00	0.12	0.99		0.05	0.95
15-15I	51.56	0.02	0.09	21.74	0.03	0.01	15.18	9.15	2.59	100.36	2.99	0.00	0.00	1.07	0.00	0.00	0.94	1.03		0.41	0.59
15-23B	50.72	0.01	0.07	26.59	<0.009	0.02	10.38	8.80	2.53	99.12	3.00	0.00	0.00	1.33	0.00	0.00	0.66	1.01		0.28	0.72
15-23B	49.94	0.03	0.09	36.08	<0.009	0.01	1.88	9.10	2.49	99.62	3.00	0.00	0.00	1.84	0.00	0.00	0.12	1.06		0.05	0.95
15-23B	50.29	<0.010	<0.04	35.55	<0.009	0.03	2.09	9.03	2.50	99.49	3.02	0.00	0.00	1.81	0.00	0.00	0.13	1.05		0.06	0.94
15-23B	49.92	0.02	0.05	36.63	<0.010	0.02	1.42	8.73	2.49	99.28	3.01	0.00	0.00	1.87	0.00	0.00	0.09	1.02		0.04	0.96
15-23B	49.55	<0.010	<0.04	36.42	0.01	0.02	2.02	9.05	2.48	99.54	2.99	0.00	0.00	1.86	0.00	0.00	0.13	1.06		0.05	0.95

A23

[illegible]

Table IV-M: Electron microprobe data for witherite in drill core SLT-015.

	Sample Number	Oxide (wt. %)							Cations calculated based on 1 CO ₃						
		MgO	FeO	MnO	BaO	CaO	SrO	CO2	Total	Mg	Fe	Mn	Ba	Ca	Sr
A24	15-23A	0.04	0.02	<0.013	75.25	<0.003	0.80	23.00	99.11	0.00	0.00	0.00	0.98	0.00	0.02
	15-23A	<0.007	<0.013	0.01	75.97	0.01	0.74	22.30	99.03	0.00	0.00	0.00	0.99	0.00	0.01
	15-23A	<0.007	<0.014	<0.013	76.77	<0.003	0.41	22.20	99.38	0.00	0.00	0.00	0.99	0.00	0.01
	15-23A	<0.007	0.02	0.03	76.37	<0.003	0.57	22.22	99.21	0.00	0.00	0.00	0.99	0.00	0.01
	15-23A	<0.007	<0.014	0.03	75.22	0.01	0.63	23.30	99.18	0.00	0.00	0.00	0.99	0.00	0.01
	15-23A	0.05	<0.013	0.04	76.17	0.01	0.51	22.80	99.58	0.00	0.00	0.00	0.99	0.00	0.01
	15-23A	<0.007	0.05	<0.013	75.05	<0.003	1.05	23.00	99.16	0.00	0.00	0.00	0.98	0.00	0.02
	15-23A	<0.007	<0.013	<0.013	75.00	0.02	0.89	23.10	99.01	0.00	0.00	0.00	0.98	0.00	0.02
	15-23A	<0.007	<0.013	<0.014	75.62	0.02	0.81	22.70	99.15	0.00	0.00	0.00	0.98	0.00	0.02
	15-23A	<0.007	0.03	<0.013	77.54	<0.003	0.93	22.00	100.51	0.00	0.00	0.00	0.98	0.00	0.02
	Average	0.04	0.03	0.03	75.90	0.01	0.73	22.66	99.33	0.00	0.00	0.00	0.98	0.00	0.01
	Std. Dev.	0.01	0.02	0.01	0.83	0.00	0.20	0.45	0.45						
	Minimum	<0.007	<0.013	0.01	75.00	<0.003	0.41	22.00	99.01						
	Maximum	0.05	0.05	0.04	77.54	0.02	1.05	23.30	100.51						

Appendix V

XRD Data for Braunite Separates

Separation of the braunite samples and subsequent XRD analysis was done using the methods outlined in Appendix III. Figure V-A shows the graphical results of the XRD analysis. These results show almost pure braunite for all six samples used in the oxygen isotope analyses.

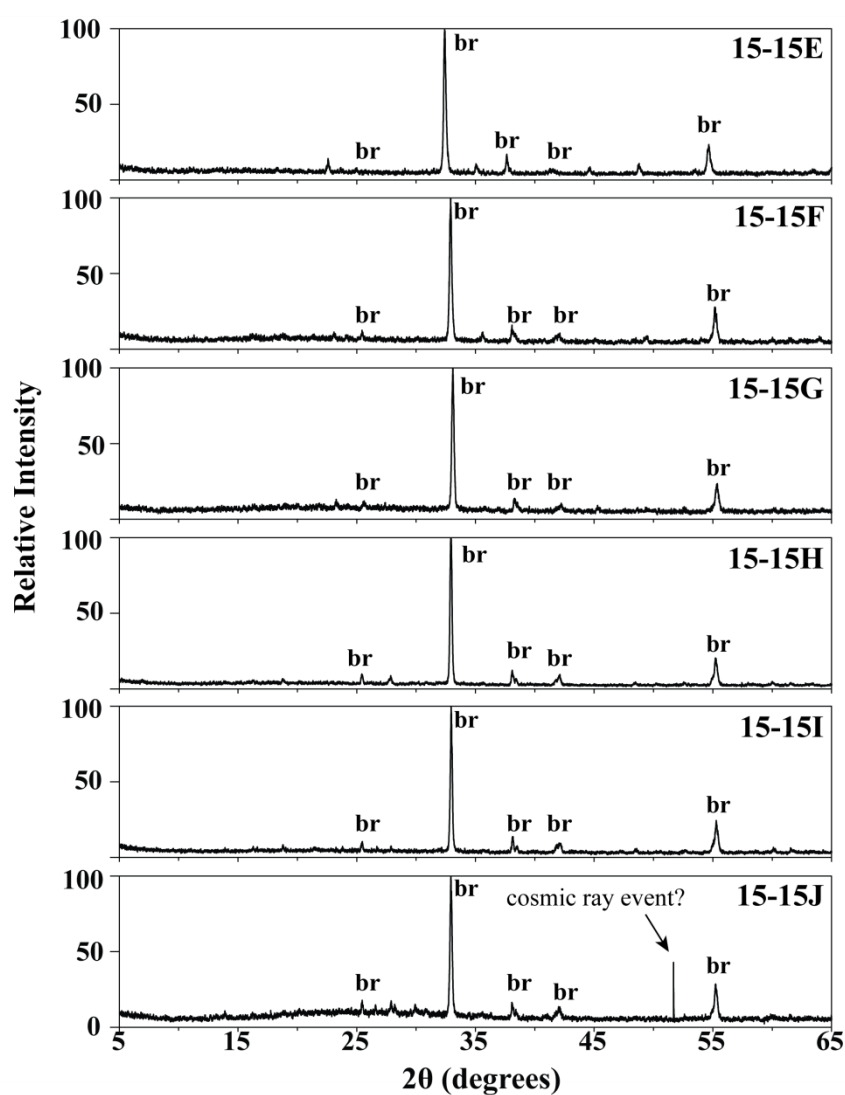


Figure V-A: XRD spectra of all samples used in oxygen isotope analyses. These spectra show essentially pure braunite with very minor contaminants in some cases.

Appendix VI

XRF Calibration Data and Detection Limits

This appendix contains XRF calibration data for major elements in Table VI-A and Table VI-B as well as error and lower limit of detection data for trace elements in Table VI-C and Table VI-D.

Table VI-A: Calibration data for XRF analyses for major elements in samples from drill core SLT-015 and AKH-49.

Oxide	Ref. disc conc. (%)	Background (%)	Count time	CPS per % oxide	Average absolute error	Average % error	Detection Limit	Reference kCPS
SiO ₂	86.641	0.304	60	578.61	0.493	0.833	0.018	50.131
TiO ₂	3.859	0.402	20	1037.82	0.012	8.159	0.026	4.005
Al ₂ O ₃	23.025	0.438	60	418.27	0.09	3.778	0.025	9.63
Fe ₂ O ₃	14.535	0.179	20	512.84	0.23	1.776	0.025	7.454
MnO	4.643	0.174	20	445.07	0.064	21.047	0.027	2.066
MgO	30.912	0.296	60	334.13	0.144	6.826	0.023	10.329
CaO	8.161	0.682	20	1448.09	0.03	0.49	0.028	11.817
Na ₂ O	9.59	0	60	449.17	0.037	2.61	0.001	4.308
K ₂ O	9.538	0.007	20	10357.6	0.017	5.461	0.001	98.791
P ₂ O ₅	2.706	0.03	60	723.03	0.007	15.558	0.005	1.956

Table VI-B: Calibration data for XRF analyses for major elements in samples from drill core SLT-017.

Oxide	Ref. disc conc. (%)	Background (%)	Count time	CPS per % oxide	Average absolute error	Average % error	Detection Limit	Reference kCPS
SiO ₂	86.436	0.216	60	575.41	0.392	0.76	0.015	49.736
TiO ₂	3.773	0.282	20	1855.09	0.012	3.586	0.017	6.999
Al ₂ O ₃	23.046	0.455	60	434.88	0.185	4.913	0.025	10.022
Fe ₂ O ₃	14.737	0.869	20	161.78	0.127	1.675	0.098	2.384
MnO	4.615	0.158	20	2279.5	0.072	16.227	0.011	10.519
MgO	29.936	0.269	60	379.53	0.042	3.762	0.021	11.362
CaO	8.178	0.528	20	203.2	0.019	0.597	0.068	1.662
Na ₂ O	10.338	0	60	681.96	0.099	6.609	0.001	7.05
K ₂ O	9.946	0.269	20	192.58	0.054	12.369	0.05	1.915
P ₂ O ₅	2.954	0.039	60	681.31	0.01	27.799	0.006	2.012

Table VI-C: Bulk geochemical trace element (transition metals) data including errors and precise detection limits.

Sample number	Zn			Cu			Ni			Co			Cr			V			Mo		
	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD
15-02	50.4	0.9	2.3	68.4	0.8	2.0	122.8	1.0	2.2	47.3	0.5	2.3	159.7	0.6	1.7	33.5	0.5	2.3	-1.1	0.3	1.0
15-08	25.5	1.3	3.8	71.4	1.2	3.1	147.2	1.6	3.6	45.4	0.8	3.5	1373.4	1.5	2.4	377.7	0.8	2.1	1.7	0.4	1.4
15-09	22.8	1.1	3.2	61.2	1.0	2.7	85.5	1.2	3.1	31.7	0.6	3.1	1068.2	1.3	2.1	252.5	0.6	1.9	0.0	0.4	1.3
15-11B	30.6	1.0	2.9	142.0	1.1	2.4	272.6	1.4	2.7	19.2	0.5	2.4	108.3	0.6	1.8	111.2	0.5	1.7	-2.8	0.3	1.2
15-15E	9.6	0.7	1.9	17.6	0.6	1.7	643.7	1.5	1.8	11.4	0.4	2.0	60.4	0.4	1.4	23.4	0.4	1.7	-0.7	0.3	0.9
15-03	152.9	2.9	7.7	1503.9	4.2	6.1	197.6	2.9	7.2	54.2	0.7	3.2	108.9	1.0	3.8	160.4	1.0	4.4	0.2	0.7	2.3
15-04	147.2	3.0	8.3	1832.2	4.7	6.4	236.3	3.2	7.9	54.9	0.8	3.5	215.5	1.1	3.8	252.7	1.0	4.1	1.8	0.7	2.4
15-13	99.6	2.9	8.2	271.3	2.7	6.4	153.1	3.0	7.8	13.4	0.8	3.8	140.7	1.0	3.8	137.3	1.0	4.2	-0.1	0.7	2.4
15-14B	70.8	3.4	9.8	137.4	2.9	7.7	229.0	3.7	9.6	22.9	1.0	4.8	126.6	1.0	3.9	120.8	0.8	3.4	2.2	0.7	2.6
15-15A	66.2	3.4	9.7	234.9	3.0	7.5	213.4	3.6	9.4	16.2	0.9	4.4	100.5	1.0	3.8	144.4	0.8	3.2	2.6	0.7	2.5
15-15B	78.2	3.4	9.6	212.2	3.0	7.5	185.7	3.6	9.3	15.8	0.9	4.4	108.8	1.0	3.8	130.4	0.8	3.1	2.3	0.7	2.5
15-24	65.7	3.0	8.8	61.6	2.5	6.8	431.0	3.7	8.6	54.0	1.3	6.2	128.4	1.1	4.2	86.4	0.8	3.3	3.2	0.7	2.4
17-14	61.5	2.8	8.1	311.4	2.7	6.3	19.7	3.4	8.6	16.2	0.8	3.7	112.6	1.0	3.9	173.5	1.0	4.2	1.2	0.6	2.0
17-15	47.6	1.9	5.5	98.9	1.7	4.3	96.9	2.6	5.8	26.2	0.8	3.7	131.3	0.9	3.4	-29.4	1.0	5.0	-0.8	0.5	1.7
17-16	45.8	2.6	7.5	95.6	2.2	5.8	59.4	3.3	8.0	27.7	0.9	4.4	152.7	1.1	4.1	-8.6	1.1	5.5	0.8	0.6	2.0
17-17	82.3	2.8	7.8	394.2	2.8	6.1	28.8	3.3	8.3	20.7	0.7	3.4	122.7	1.0	3.7	242.4	1.0	4.0	2.3	0.6	2.0
17-18	61.2	2.1	6.0	176.8	2.0	4.7	105.4	2.8	6.3	27.8	0.7	3.4	124.4	1.0	3.6	26.6	1.0	4.9	0.9	0.5	1.8
17-19	65.2	2.4	6.8	95.1	2.0	5.3	25.3	2.9	7.3	6.8	0.7	3.4	117.6	1.0	3.7	78.3	1.0	4.6	1.7	0.5	1.9
49-S	1.6	0.1	0.3	6.7	0.2	0.2	11.3	0.2	0.3	26.4	0.4	1.9	276.8	0.7	1.6	28.3	0.5	2.3	-0.7	0.3	1.0
49-G	2.5	0.2	0.4	9.5	0.2	0.3	16.6	0.3	0.4	55.4	0.6	2.7	63.0	0.6	2.3	-15.7	0.8	3.8	-1.9	0.4	1.2
49-1	74.2	1.3	3.6	53.3	1.1	3.0	1371.0	3.0	3.4	90.5	0.6	2.5	82.2	0.6	2.0	20.5	0.4	1.9	1.4	0.4	1.4
49-4	44.0	1.0	2.7	27.5	0.8	2.3	295.3	1.4	2.5	50.0	0.6	2.7	47.5	0.6	2.4	-41.0	0.8	4.0	-3.9	0.3	1.2
49-7	2.0	0.2	0.4	9.1	0.2	0.3	15.8	0.3	0.4	61.6	0.6	2.7	50.9	0.6	2.3	-26.8	0.8	3.8	-1.8	0.3	1.2
49-12	1.9	0.1	0.3	7.3	0.2	0.3	13.0	0.3	0.4	59.0	0.5	2.4	54.8	0.5	1.8	5.2	0.5	2.5	-0.2	0.3	1.0

Table VI-C: Bulk geochemical trace element (remaining elements) data including errors and precise detection limits.

Sample number	Sc			Th			Pb			Rb			Nb			Zr			Y			U			Sr		
	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD	ppm	Err.	LLD
15-02	40.0	0.2	0.5	33.1	0.7	2.5	35.1	0.9	2.8	55.9	0.5	1.0	21.6	0.3	0.9	233.4	0.6	1.0	40.4	0.3	1.0	1.5	0.5	1.9	501.3	0.9	1.0
15-08	57.9	0.3	0.5	9.6	1.0	3.5	76.4	1.2	3.9	49.2	0.7	1.5	8.3	0.4	1.3	142.0	0.7	1.3	12.3	0.4	1.4	1.8	0.8	2.7	156.1	0.8	1.4
15-09	65.7	0.3	0.5	6.7	0.9	3.1	77.6	1.1	3.5	51.2	0.6	1.3	8.0	0.3	1.1	140.0	0.6	1.2	16.3	0.4	1.3	-1.4	0.7	2.4	101.0	0.6	1.3
15-11B	20.9	0.2	0.4	31.7	0.9	2.9	44.8	1.0	3.3	62.7	0.6	1.2	26.1	0.3	1.1	571.4	1.0	1.1	58.5	0.4	1.2	2.1	0.6	2.2	71.0	0.6	1.2
15-15E	8.0	0.2	0.4	16.9	0.6	2.1	120.8	0.8	2.4	97.3	0.5	0.9	13.2	0.2	0.8	130.4	0.4	0.8	95.8	0.3	0.9	-0.6	0.5	1.6	119.3	0.5	0.9
15-03	50.9	0.4	0.9	2.8	1.7	5.7	250.8	2.3	6.6	0.2	0.9	2.4	2.9	0.6	2.1	46.3	0.8	2.2	18.8	0.7	2.3	1.1	1.3	4.4	487.8	1.8	2.4
15-04	117.3	0.5	0.8	9.1	1.7	5.9	548.5	2.8	6.8	2.4	0.9	2.5	3.0	0.6	2.2	61.3	0.9	2.3	20.5	0.7	2.4	-0.3	1.3	4.5	380.9	1.7	2.5
15-13	10.8	0.3	0.8	14.2	1.7	5.9	1003.0	3.3	6.8	33.3	1.0	2.5	0.9	0.6	2.2	34.2	0.8	2.3	24.4	0.7	2.4	-2.8	1.3	4.6	2164.9	3.5	2.5
15-14B	2.3	0.3	0.8	4.6	1.8	6.4	503.2	2.9	7.2	3.6	1.0	2.7	2.1	0.7	2.3	11.1	0.8	2.4	46.3	0.8	2.6	-0.7	1.4	4.9	521.4	2.0	2.6
15-15A	5.8	0.3	0.7	3.2	1.8	6.3	387.0	2.7	7.2	1.9	1.0	2.7	1.2	0.7	2.3	16.0	0.8	2.4	29.5	0.8	2.5	0.1	1.4	4.8	377.1	1.7	2.6
15-15B	6.3	0.3	0.7	7.8	1.8	6.3	410.4	2.8	7.2	0.0	1.0	2.7	0.3	0.7	2.3	14.3	0.8	2.4	26.8	0.8	2.6	-0.2	1.4	4.8	473.7	1.9	2.6
15-24	7.6	0.3	0.8	0.2	1.7	6.0	179.1	2.3	6.8	62.6	1.1	2.5	4.4	0.6	2.1	42.9	0.9	2.3	56.2	0.8	2.4	1.8	1.3	4.5	203.6	1.3	2.4
17-14	11.6	0.3	0.8	14.9	1.4	4.8	968.3	3.0	5.6	3.1	0.8	2.2	2.0	0.6	2.0	20.6	0.7	2.0	18.3	0.7	2.2	0.2	1.0	3.6	1462.6	2.8	2.2
17-15	25.8	0.3	0.8	63.6	1.2	3.9	2677.2	3.8	4.5	9.9	0.7	1.7	15.9	0.5	1.6	344.3	1.1	1.6	48.8	0.6	1.7	0.4	0.8	2.9	1313.4	2.2	1.7
17-16	18.9	0.3	0.9	43.3	1.4	4.7	2660.6	4.4	5.6	6.4	0.8	2.1	11.4	0.6	1.9	82.5	0.8	1.9	18.4	0.6	2.1	1.4	1.0	3.5	1184.3	2.5	2.1
17-17	18.3	0.3	0.7	22.6	1.4	4.7	1440.5	3.4	5.5	4.9	0.8	2.1	4.6	0.6	1.9	57.8	0.8	1.9	36.1	0.7	2.1	1.2	1.0	3.5	361.1	1.5	2.1
17-18	29.2	0.3	0.8	46.7	1.3	4.1	2254.8	3.7	4.8	15.5	0.7	1.8	12.4	0.5	1.7	245.4	1.0	1.7	30.4	0.6	1.8	4.6	0.9	3.1	947.0	2.0	1.8
17-19	8.1	0.3	0.9	19.3	1.3	4.4	1201.5	3.1	5.2	2.1	0.7	2.0	2.1	0.5	1.8	23.4	0.7	1.8	8.5	0.6	2.0	2.3	1.0	3.3	1699.5	2.8	2.0
49-S	23.9	0.2	0.5	24.0	0.7	2.3	156.4	0.9	2.6	127.7	0.6	1.0	23.0	0.3	0.8	256.7	0.6	0.9	60.0	0.3	0.9	0.9	0.5	1.7	200.9	0.6	0.9
49-G	16.0	0.3	0.7	27.5	0.9	3.0	991.3	1.9	3.4	92.8	0.6	1.2	15.4	0.0	1.1	274.6	0.7	1.2	46.9	0.4	1.2	0.2	0.7	2.3	263.9	0.8	1.2
49-1	19.4	0.2	0.5	14.7	1.0	3.4	589.5	1.8	3.9	12.8	0.6	1.4	7.2	0.4	1.2	100.2	0.6	1.3	107.0	0.5	1.4	2.4	0.7	2.6	94.4	0.7	1.4
49-4	10.2	0.3	0.7	22.5	0.8	2.8	885.2	1.7	3.3	95.5	0.6	1.2	14.1	0.3	1.1	283.5	0.7	1.1	105.1	0.5	1.2	-0.4	0.6	2.2	181.1	0.7	1.2
49-7	9.0	0.3	0.7	26.9	0.9	2.9	1161.9	1.9	3.3	98.8	0.6	1.2	15.8	0.3	1.1	280.0	0.7	1.1	113.6	0.5	1.2	-1.9	0.6	2.2	175.7	0.7	1.2
49-12	13.3	0.2	0.5	21.0	0.8	2.5	575.8	1.4	2.9	117.1	0.6	1.1	14.7	0.3	0.9	258.2	0.6	1.0	75.7	0.4	1.0	-0.1	0.6	1.9	84.4	0.5	1.0