



# **The petrogenesis and geochemistry of the Namaqualand olivine melilitite pipe cluster, western South Africa.**

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**By: Michael Dominic Kirchner**

mdkirchner@gmail.com

Department of Geological Sciences

University of Cape Town

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**Supervisor: Dr. P. E. Janney**

[phil.janney@uct.ac.za](mailto:phil.janney@uct.ac.za)

Department of Geological Sciences

University of Cape Town

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**MSc Thesis Title: The Petrology and Geochemistry of the Olivine Melilitite pipes in  
Namaqualand South Africa.**

By M. D. Kirchner<sup>1</sup> & supervised by P. E. Janney<sup>2</sup>

1. MSc Student in Department of Geological Sciences, University of Cape Town, South Africa.

mdkirchner@gmail.com

2. Lecturer in Department of Geological Sciences, University of Cape Town, South Africa.

phil.janney@uct.ac.za

Name: Michael Kirchner

Student Number: **KRCMIC 003**

Course: MSc in GEOLOGY

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## ABSTRACT:

The Namaqualand olivine melilitite pipe cluster is a 40 km by 10 km north/south oriented area with at least 10 closely spaced alkaline ultramafic subvolcanic pipes and diatremes containing olivine melilitite and nephelinite, spanning an age range of 35-56 Ma. A related carbonatite complex containing olivine melilitite is also found within this cluster, with an emplacement age of  $\approx 55$  Ma. The Namaqualand cluster represents the southernmost component of the Late Cretaceous to Paleogene-age Namaqualand-Bushmanland-Warmbad (NBW) lineament, representing a 400 km long NNE-SSW trending feature made of hundreds of diatremes containing ultramafic lamprophyre and kimberlite in addition to the rock types named above. The NBW lineament appears to be an age-progressive feature, with ages increasing toward the northeast at a rate and direction roughly consistent with Late Cretaceous to Cenozoic African plate motion. This suggests that it could have formed from a single source, such as a mantle plume, with the earlier products being the Warmbad kimberlites, followed by the later diatremes of the Bushmanland cluster and the youngest being the Namaqualand olivine melilitites. This study focuses on the petrography and geochemistry of fresh igneous rocks sampled from 10 pipes in the Namaqualand cluster. The samples have unusual compositions for diatreme-hosted alkaline igneous rocks in that they are relatively differentiated, with whole rock Mg numbers of between 71 and 45. This suggests that many of these samples represent magmas that evolved through more than 50% fractional crystallization of mineral assemblages dominated by olivine but also containing significant melilite, nepheline, phlogopite, titanomagnetite and perovskite. However, least-squares fractionation modelling appears to only provide an approximate guide to the fractionating mineral assemblages. The concentrations of most incompatible trace elements in the Namaqualand melilitites are relatively uniform, suggesting a common source and petrogenesis. Low Pb concentrations in the Namaqualand melilitites, along with their  $\text{SiO}_2$ - and  $\text{Al}_2\text{O}_3$ -poor major element compositions make it unlikely that they experienced significant (e.g., more than 5-10%) assimilation of local continental crust. The Namaqualand melilitites are characterized by extraordinarily high and variable Nb/Rb and U/Th ratios, and correlations with other elements indicate that these ratios have been affected by variable fractional crystallization of phlogopite and perovskite, respectively. However, this cannot explain the unusually high U concentrations and low Th/U ratios of the most primitive Namaqualand melilitites, which appear to be a source feature. Oxygen isotope ratios of olivine separates indicate that olivines from a large majority of the melilitite pipes have compositions indistinguishable from those from typical upper mantle peridotite (4.9-5.2‰). However, three melilitite pipes emplaced within the mid-Cretaceous Koegel Fontein igneous complex contain olivines with exceptionally low  $\delta^{18}\text{O}$  values (i.e., down to +4.2 ‰). The crustal country rock surrounding the Koegel Fontein complex, as well as igneous rocks strongly contaminated by this crust, have exceptionally low  $\delta^{18}\text{O}$  values (down to -4 and -5.3‰, respectively). The unusually low  $-\delta^{18}\text{O}$  values of these olivines could be explained by the assimilation of up to 10% of Koegel Fontein country rock crust having the lowest  $\delta^{18}\text{O}$  values measured. Larger amounts of crustal assimilation are

not plausible as they would result in detectable increases in  $\text{SiO}_2$  and Pb/Ce ratios. It is unclear whether the crustal assimilation detected in the melilitites emplaced within the Koegelfontein complex is typical of most Namaqualand melilitites. The Namaqualand melilitites have radiogenic isotope compositions that overlap with those of melilitites and kimberlites from the Bushmanland and Warmbad clusters, as well as with southern African Group I kimberlites. However, the Namaqualand pipes are unique in that some samples have radiogenic isotope values approaching those of HIMU oceanic island basalts (e.g., from St. Helena, Mangaia, Tubuai), whereas the Bushmanland and Warmbad clusters display isotopic compositions that only extend to weaker HIMU signatures. The geochemical and age-distance patterns displayed by the NBW igneous rocks are most consistent with the action of a mantle plume passing beneath the western margin of southern Africa in the Late Cretaceous to Paleogene, resulting in the generation of the NBW lineament. This is consistent with the fact that the samples with the strongest HIMU signatures in the NBW lineament are those that have been emplaced on the thinnest lithosphere, nearest the continental margin. The HIMU signature dominant in the Namaqualand melilitites is presumably related to the plume source, which could contain ancient recycled oceanic crust. The formation of the African megalineament could theoretically be related to the same plume that caused the NBW lineament by triggering a zone of magmatism along a deep-seated zone of weakness in the lithospheric mantle between Southern Africa into the east African rift zone, however, more evidence would be needed to fully support this possibility.

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# 1. INTRODUCTION:

Mafic alkaline magmatism is widespread across the African continent in the form of kimberlites and other silica-undersaturated, potassic and carbonatitic magma types (e.g., Sykes, 1978; Woolley, 2001). On the western half of the African plate, there is a strong association between alkaline magmatism and recorded intraplate seismicity, reactivation of pre-existing zones of weakness and other tectonic activity like faulting that post-date the main period of Gondwana continental fragmentation. The location of these features has been depicted in Figure 1 (Woolley, 1978, Moore *et al.*, 2008).

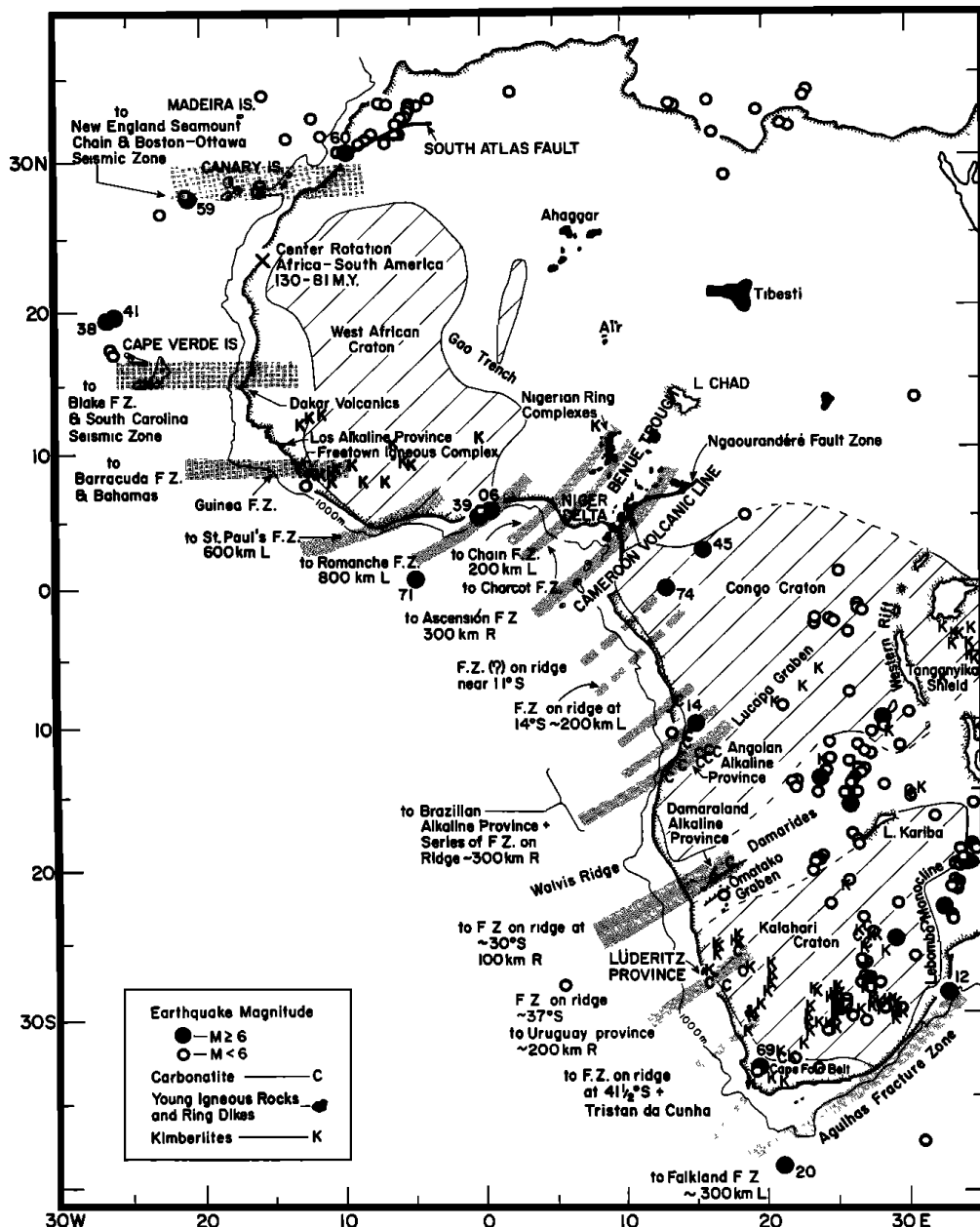


Figure 1: The location of earthquakes as well as alkaline igneous rocks along the Atlantic margin of northern and southern Africa, after Sykes (1978), which shows a common trend of seismic activity and alkaline volcanism lying along a north-easterly orientation approximately parallel with the direction of African plate motion.

The origin of the alkaline magmatism along the west coast of Africa has been more extensively studied in southern Africa, however, it has not yet been completely explained by plate tectonic processes (e.g., Ashwal & Burke, 1989; Burke, 1996; Moore *et al.*, 2008).

Some of these manifestations of alkaline magmatism are age-progressive and could be explained by plume activity, while others lack the temporal-spatial patterns expected from mantle plumes (e.g., Jelsma *et al.*, 2009). Therefore, these occurrences of alkaline magmatism in southern Africa have drawn significant research interest but have not yet been comprehensively explained. This is one reason why further study of these occurrences of magmatism in Southern Africa has significant importance to our understanding of geological history and magmatic processes. This region of magmatism in southern Africa provides a key to understanding the larger phenomenon of these occurrences of alkaline magmatism found along the entire west coast of Africa and its relationship with the Earth's tectonic history as well as the magmatism in the interior portions of the African craton.

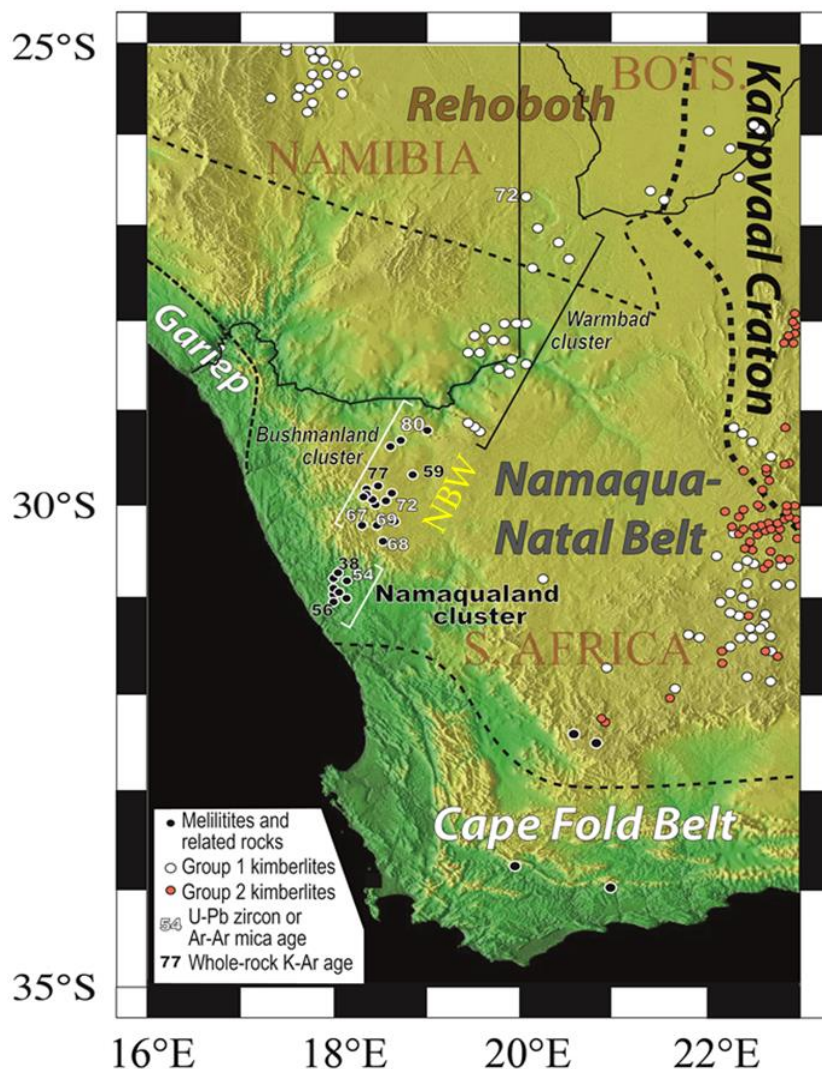


**Figure 2.** Map showing the western part of South Africa and Southern Namibia with the location of the Late Cretaceous/Tertiary NBW magmatic lineament consisting of the Namaqualand, Bushmanland and Warmbad magmatic clusters as well other widely spaced alkaline rocks of a similar recent age (modified after Janney *et al.*, 2017).

This study examines an aspect of this alkaline magmatism by studying the geochemistry and petrology of a cluster of vertically oriented, pipe-shaped sub-volcanic features in the Namaqualand region on the western margin of South Africa (Figure 2). Although emplaced in a less explosive fashion, the ten pipes studied appear to represent the root zones of diatremes, somewhat akin to kimberlites (Moore and Verwoerd, 1985). These pipes have experienced significant erosion, likely due to regional uplift (Moore, 1979). The sub-volcanic, hypabyssal igneous rocks now exposed (dominantly olivine melilitite and olivine nephelinite) have yielded a suite of petrographically and geochemically similar samples (Moore, 1979; Janney *et al.*, 2002; Moore *et al.*, 2009).

The term “pipe” is used here to denote any vertically oriented, roughly cylindrical or conical magmatic body including diatremes and hypabyssal/subvolcanic pipe-shaped intrusions. The Namaqualand cluster of pipes forms the south westernmost member of the “Namaqualand-Bushmanland-Warmbad” (NBW) province, which is an age-progressive magmatic lineament that is composed of hundreds of melilitite, nephelinite and kimberlite diatremes, extending from Namaqualand near the west coast of South Africa, through the Bushmanland Plateau to the Gordonia region of NW South Africa as well as the Warmbad region in of south-eastern Namibia (Moore and Verwoerd, 1985; Janney *et al.*, 2002; Janney *et al.*, 2003; Skinner *et al.*, 2007; Moore *et al.*, 2008; Day *et al.*, 2014; Moore, 1973; Figure 2).

The NBW province also appears to represent the southwestern-most extension of a larger magmatic “megalineament” of more diffuse alkaline magmatism (mainly kimberlites) extending 2500 km to north-eastern Zambia, almost to the southern tip of the East African Rift System (EARS) as depicted in Figure 3 (Moore *et al.*, 2008; Janney *et al.*, 2017; Jelsma *et al.*, 2004). This lineament is of interest for understanding the tectonic history and current status of tectonic activity beneath the African plate as its occurrence may correspond to a broader tectonic feature such as an early stage of continental rifting or a large-scale tectonic zone of weakness/deformation that has yet to be fully described (Moore *et al.*, 2008; Jelsma *et al.*, 2004). Further work towards unravelling this enigmatic feature is, therefore, of scientific interest and value.

There are several other roughly northeast-southwest-aligned alkaline magmatic lineaments (Figure 1) that cross the southwestern continental margin of Africa (Sykes, 1978). In some cases, they are age-progressive as they increase in age to the northeast along the lineament (e.g., the Late Cretaceous-Paleogene Western Cape melilitites of South Africa; Janney *et al.*, 2002; and the Gibeon-Dicker Willem-Schwarzeberg lineament of southern Namibia; Reid *et al.*, 1990; Spriggs, 1988). In other cases, there is no apparent age progression (e.g., the Cambrian Kuboos-Bremen Line of southernmost Namibia and NW South Africa; Reid *et al.*, 1991; the Early Cretaceous Damaraland intrusive complexes of NW Namibia; Milner *et al.*, 1995; Cretaceous-age Angolan kimberlites of the “Lucapa corridor”; e.g., Robles-Cruz *et al.*, 2012). These features may offer a clue to the location of a larger-scale zone of weakness activated during or after the break-up of Gondwana (Sykes, 1978; Jelsma *et al.*, 2004, Moore *et al.*, 2008). The origin(s) and source location(s) of the mantle source(s) for the magmas that produce these lineaments, and specifically the NBW lineament, are still uncertain.

The possible explanations for this type of low-volume alkaline magmatism include (1) incipient continental extension (in contrast to full-fledged continental rifting; Jelsma *et al.*, 2004; Moore *et al.*, 2008), (2) edge-driven asthenospheric convection (King and Anderson, 1998; King and Ritsema, 2000), or (3) the product of one or more mantle plumes beneath a north-easterly moving African plate (e.g., Duncan, 1981). The presence of the NBW alkaline magmatic province, formed between about 38 and 90 Ma and the larger “megalineament” inferred by Moore *et al.* (2008) extending across southern Africa, of which it may be a part, suggests the existence of a geologically recent deep anomaly of some kind in the mantle beneath southern Africa. The possible origins of such an anomaly have already received much discussion (e.g., Marsh, 1973; Moore, 1976; Moore and Verwoerd, 1985; Rogers *et al.*, 1992, Moore *et al.*, 2008; Janney *et al.*, 2002; 2017), but this remains uncertain and in current debate.

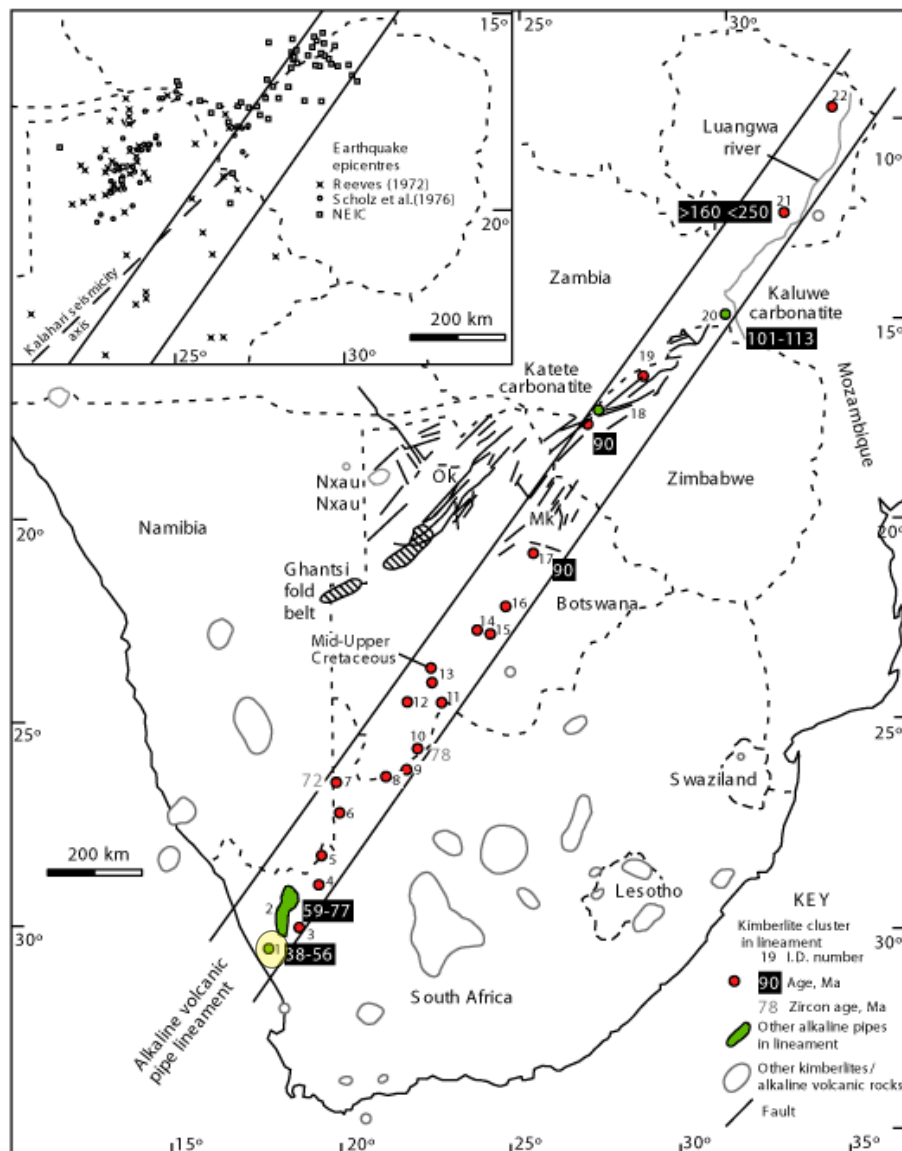


**Figure 3. Diagram illustrating how the NBW lineament may form part of a larger cross-continental lineament or transcontinental “alkaline volcanic pipe lineament” of kimberlitic and related deeply sourced magmatism which is indicative of an early stage of continental rifting or some other major tectonic event (After Jelsma *et al.*, 2004). The Namaqualand cluster (1) is highlighted in yellow.**

This study, which focuses on the petrology and geochemistry of rocks sampled from ten of the melilitite pipes in the Namaqualand cluster of the NBW lineament, provides a unique opportunity to improve our understanding of this unusual lineament. While broadly similar in mineralogy and geochemistry, these pipes also show significant variations in major and trace-element and radiogenic isotope composition that may provide crucial information on the sources and petrogenesis of this cluster of melilitites. Compared to samples of the much more numerous melilitite pipes of the Bushmanland cluster to the northeast, the Namaqualand melilitites show a significantly greater compositional range in major and trace elemental and radiogenic isotopic composition. The comparatively large compositional variations shown by the Namaqualand melilitite cluster are possibly related to three factors which are: (1) it being located closest to the continental margin and (presumably) on the thinnest lithosphere of the three NBW magmatic clusters and (2) it having been emplaced within two distinct crustal types: (a) Mesoproterozoic gneisses of the Namaqualand Metamorphic Complex and (b) Early Cretaceous igneous rocks of the Koegelfontein Complex (see Chapter 2). Finally, (3) it having experienced greater degrees of fractional crystallization of olivine as well as potential olivine accumulation.

### **1.1. Motivations for this study:**

There are a number of different factors that justify a new study of the Namaqualand melilitite cluster. Some of these are:

1. A larger number of pipes (10) have been sampled and all samples are accurately located by GPS. Previous studies sampled a smaller number of pipes ( $\approx 5$ ) and none were accurately geolocated.
2. These new samples show a significantly greater extent of geochemical variation, including more diverse source signatures, and evidence for more extensive fractional crystallization than was previously predicted.
3. The types of geochemical measurements obtainable are more diverse, including high precision trace element measurements by ICP-MS and Hf and O isotope ratio measurements. These high precision measurements are crucial for better understanding the sources, petrogenesis and ultimate origins of the Namaqualand melilitites and for comparison with related rock types.
4. An increased number of geochronological data points for igneous rocks of the NBW lineament (e.g., Griffin *et al.*, 2014; Stanley and Flowers, 2015), has provided additional evidence for age-progressive magmatism. This makes the understanding of the origin of the NBW lineament more crucial to understanding this phenomenon common to the west coast of Africa.

A further significant reason for this study is the geochemical evidence that, as originally pointed out by Moore (1979) and Rogers *et al.* (1992), the rocks of the Namaqualand melilitite cluster are unusually Mg-poor and Fe- and Ti-rich, with Mg# ( $\text{Mg} / [\text{Mg} + \text{Fe}^{2+}] * 100$ ) values typically in the range of 50 to 65, which is unusually low compared both to igneous rocks in the Bushmanland and

Warmbad diatreme clusters, as well as to diatreme-hosted igneous rocks globally (with Mg# values typically of 70 to 80). These authors proposed that the Namaqualand melilitites represented primary magmas (which must normally have Mg numbers of at least 70 to be in equilibrium with mantle olivine) but that their Fe-rich compositions were the result of unusually CO<sub>2</sub>-rich and/or reducing conditions in their mantle sources (Moore and Erlank, 1979; Rogers *et al.*, 1992). However, the large change in Fe/Mg partitioning that would be required in this scenario has not been supported by subsequent experimental data at varying oxidation states and carbon dioxide activities (Beattie, 1993; Putirka *et al.*, 2007; Davis and Cottrell, 2021).

Subsequent investigations have suggested that the Namaqualand melilitites have experienced up to 50% fractional crystallization, with fractionating assemblages dominated by olivine (Janney *et al.*, 2002; Janney *et al.*, 2003; 2017). If correct, the presence of such highly fractionated magmas occurring in diatremes poses a major problem for understanding their origin, given that virtually all igneous rocks occurring in diatremes elsewhere (including the nearby Bushmanland and Warmbad clusters) have compositions approaching those of primary magmas suggesting a rapid ascent from the mantle driven by the rapid expansion of exsolving volatiles (Janney *et al.*, 2017).

## **1.2. Aims and scope of this study:**

The main aims of this thesis are to present a comprehensive petrographic and geochemical survey of the Namaqualand melilitite cluster to help explain its petrogenesis, characterise its mantle source(s) and constrain its ultimate origin. This study is based on an analysis of a collection of samples obtained from 10 pipes located across the cluster, with a focus on collecting and analysing the freshest material available. For this study, 30 samples were newly collected from 9 pipe localities in the Namaqualand region, additionally, data for olivine melilitite samples from the Zandkopsdrift carbonatite (Ogunbuyi, 2019) have also been included. The samples collected were petrographically described, and analysed for their mineral and whole rock major and trace element compositions, as well as their radiogenic isotope compositions. The oxygen isotope compositions of olivine separates were also obtained. This study compares new and old data previously obtained for samples from the Bushmanland cluster, as well as the Namaqualand cluster to better understand petrogenetic and source region differences between these pipe clusters.

In addition to providing an improved characterisation of the geochemistry of the Namaqualand melilitite pipes and better constraints on their petrogenesis and tectonic origin, this thesis will address the following specific questions:

1. What was the mineralogy of the mantle source(s) and the conditions of melting (i.e., degree and depth of melting) involved in the generation of the Namaqualand melilitites, and how do these compare with those inferred for the neighbouring Bushmanland melilitites?

2. To what extent have the Namaqualand melilitites been affected by crustal assimilation? Can differences be observed in the elemental, radiogenic isotope or oxygen isotope compositions between pipes/samples emplaced within the Cretaceous Koegelfontein complex versus those emplaced in the Proterozoic Garies Terrane of the Namaqua-Natal mobile belt?
3. What are the specific constraints that can be placed on the composition of the various mantle source(s) contributing to the Namaqualand melilitites, as well as the nature of any mixing systematics? The likely physical locations of the source(s) identified will also be discussed.
4. What is the differentiation history of the Namaqualand melilitites? What is the range of extent of fractional crystallization, and which minerals are included in the fractionating assemblages? Can any explanation be found for the occurrence of relatively fractionated igneous rocks in a diatreme setting?

This study applies geochemical techniques and isotopic methods that have not been previously applied to these rocks to a wider range of localities than has previously been examined. Therefore, this study builds on previous work and represents a significant step forward by providing new insights into this enigmatic cluster of unusual igneous rocks which is also one of the densest concentrations of mafic alkaline magmatism in southern Africa (Skinner *et al.*, 1992, Skinner *et al.*, 1997).

## 2. GEOLOGICAL BACKGROUND:

### 2.1. What are olivine melilitites?

By definition, olivine melilitites are igneous ultramafic rocks, typically extrusive, containing coarse to medium-grained olivine phenocrysts, as well as microphenocrystic and/or groundmass olivine, melilite, clinopyroxene, nepheline. Additionally, they are known to contain oxide minerals such as titanomagnetite, perovskite, ilmenite and occasionally also phlogopite (Le Maitre *et al.*, 2005). The most characteristic modal mineral in this rock type is melilite and they have been defined as rocks with >10 % modal melilite when called melilitites *sensu stricto* (Le Maitre, 2002). Olivine melilitites are melilitites that contain more than 10 % modal olivine (Le Maitre, 2002). Extrusive rocks with similar mineralogy but having less than 10 % modal melilite are defined as nephelinites (Moore, 1979; Le Maitre *et al.*, 1989). The nephelinites with more than 10 % olivine are defined as olivine nephelinites (Moore, 1979).

From earlier studies, some samples from the Namaqualand/Bushmanland region, sub-solidus replacement of melilite by clinopyroxene has resulted in the formation of medium-grained clinopyroxene-rich olivine nephelinites (Verwoerd and de Beer, 2006). Some varieties showing predominant clinopyroxene and low amounts of melilitite have been called melilitite-bearing pyroxenites due to the sheer abundance of pyroxene (Moore, 1979). In this study, both the coarse and fine-grained melilite-free varieties are referred to as nephelinites as they may be chemically indistinguishable.

A continuous series exists from olivine melilitites to olivine nephelinites to nephelinites (Le Maitre *et al.* 1989) but it is difficult to confidently classify the rocks into these categories by modal mineralogy as they become finer-grained, or where the original melilite has been replaced by clinopyroxene (Moore, 1979). Therefore, it is advantageous to consider the normative mineralogy and geochemistry of these rocks as additional means for their classification (Le Maitre, 2002; Le Maitre *et al.*, 2005).

From a historical perspective, the term “olivine melilitite” is a petrological term that has often been used to describe a wider range of rocks with types/textures ranging from olivine melilitite *sensu stricto* to olivine-nepheline melilitite, olivine nephelinite, monticellite peridotites and other mineralogical/textural varieties of similar composition or appearance which have a fine-grained dark grey to a black crystalline matrix and often, but not always, contain olivine phenocrysts (Verwoerd and de Beer, 2006; Moore, 1979). It is often challenging to accurately distinguish these different varieties in the field. Therefore, many rocks originally identified as “olivine melilitites”, prove later to contain less than the 10 modal percent melilite necessary to be strictly classified as melilitites (Verwoerd and de Beer, 2006).

The most likely reason for the broad application of the term “olivine melilitites” is because olivine melilitites are generally the most common rock type found that has a similar appearance. In

this study, the broader definition of “olivine melilitites” and “melilitites” is used in a similar manner as indicating fine-grained porphyritic olivine, melilitite and clinopyroxene bearing volcanic or sub-volcanic rocks that share a common macroscopic appearance. However, ideally it should be made clear when the term “melilitite” is being used in this looser sense or more strictly as defined by the IUGS (i.e., >10% modal melilitite, Le Maitre *et al.*, 2002).

## 2.2. Melilitites and South African alkaline magmatism.

Across Africa, a large variety of relatively young (i.e., post-Gondwana) silica undersaturated magmatic rocks has been identified (e.g. Sykes, 1978). These are regarded as anomalous features of significant interest to understanding the geology of the African continent. Many of these magmatic bodies, most commonly kimberlites, carbonatites and various ultramafic to felsic alkaline igneous rocks, appear within magmatic lineaments (i.e., linear features along which magmatism appears to be concentrated). A few hypotheses have been proposed to explain these linear features including:

1. The Cretaceous to Cenozoic north-easterly movement of the African plate over mantle plumes (e.g., le Roex, 1986; Duncan, 1981; Reid *et al.*, 1990; Sykes, 1978; Woolley, 2001), which results in cross-continental linear magmatic features that, in some cases, may be traced to related volcanism found within the Atlantic Ocean crust e.g., Cameroon Line, Vema/Discovery trail, Damaraland intrusive complexes with Walvis Ridge and Tristan.
2. Edge-driven convection along the margins of the African continent, caused by the temperature contrast between the asthenosphere and lithosphere of variable thickness (King and Ritsema, 2000).
3. Lines of structural weakness, possibly related to the inland extension of fracture zones, lithospheric shear zones or incipient rifting, where magmatism is concentrated (Marsh, 1973, Moore, 1976; Moore *et al.*, 2008; Jelsma *et al.*, 2004).

Whatever the cause of these magmatic lineations, it is important to note that this study focuses on only a relatively small sampling area within the Namaqualand melilitite cluster. The origin and petrogenesis of Namaqualand melilitites are of significant scientific interest. This is due to the fact that, firstly, they are part of the  $\approx 400$  km-long NBW magmatic province, and possibly part of a more diffuse  $\approx 2500$  km lineament extending across southern Africa to the southern East African Rift (Moore *et al.*, 2008). Secondly, the NBW province is only one of three NE-SW oriented, Late Cretaceous to Palaeogene age alkaline magmatic lineaments crossing the south-western African margin, which makes them unusual.

Southern Africa contains numerous occurrences of Mesozoic to Cenozoic olivine melilitites, kimberlites and other alkaline and silica undersaturated intraplate magmas, including olivine melilitites, carbonatites, kimberlites, nephelinites, alkali basalts, and more differentiated rock types such as phonolites, trachytes and nepheline syenites that are shown in Figure 4 (Taljaard, 1936; Taljaard 1937; Verwoerd and De Beer, 2006; Moore *et al.*, 1976; Moore *et al.*, 2008). While they span a wide range of ages from Proterozoic to recent, they are particularly dominant in the Mesozoic and

Cenozoic (Woolley, 2001). Along the south-western coast of Africa, these are concentrated in three distinct northeast-southeast oriented linear groupings of 300 to  $\geq 500$  km in length that is at least roughly age-progressive with ages increasing toward the northeast (e.g., Duncan, 1981; Moore and Verwoerd, 1985; Moore *et al.*, 2008; Griffin *et al.*, 2014). From south to north they are:

### **1. The Western Cape Melilitite Province:**

The 58-76 Ma Western Cape Melilitite Province lineament consists of (from south to north): (a) submarine alkaline basalts and trachytes of the Alphonse Bank, on the continental shelf SE of Cape Agulhas (Dingle and Gentle, 1972) (b) The Robertson and Heidelberg melilitite localities in the southern Western Cape consisting of at least 7 melilitite pipes (Gerrard, 1958; Viljoen and Verwoerd, 2006), (c) the Sutherland Commonage melilitite complex consists of one or two sills surrounded by an annular ring dyke or cone sheet (Gerrard, 1958; Viljoen, 1988) and (d) the Saltpeterkop carbonatite/trachyte/melilitite complex (Verwoerd, 1990), containing dykes, sills and pipes of olivine melilitite, as well as carbonatite and ultramafic lamprophyre, are both located near the town of Sutherland in the Northern Cape. Possible links to the Victoria West kimberlite field further to the northeast have been suggested (Chevallier, 1997). The age-distance relationship in the western cape melilitites is consistent with the estimated speed of African plate motion, however, the orientation of the lineation is off by about  $30^\circ$  as the western cape melilitite province is nearly N-S whereas African plate motion is more north-eastward which makes matching the path of the African plate motion with the lineament problematic.

### **2. The Namaqualand-Bushmanland-Warmbad lineament:**

The Namaqualand-Bushmanland-Warmbad (NBW) lineament has been dated at  $\sim 38$  to 80 Ma (Skinner, 1997, Moore *et al.* 2008). The lineament consists of three clusters aligned roughly  $35^\circ$  east of north. From southwest to northeast these are the Namaqualand melilitite cluster (containing  $\sim 10$ -12 pipes), the larger and denser Bushmanland melilitite cluster (consisting of more than 300 pipes) and the even larger but more diffuse Warmbad kimberlite cluster (consisting of approximately 50 known pipes over nearly 200 km of linear distance) (Moore and Verwoerd, 1985). The Bushmanland cluster includes  $\sim 25$ -35 pipes containing fresh olivine melilitite and the remainder is filled with either sediment or volcanoclastic breccia (Moore and Verwoerd, 1985). The Warmbad cluster consists of approximately 50 Group 1 kimberlite and ultramafic lamprophyre diatremes extending from northern Bushmanland to northern Gordonia, and including a significant number in the south-eastern corner of Namibia (Skinner *et al.*, 1992; Skinner *et al.*, 1997; Skinner., 2009; Verwoerd and de Beer, 2006). There are possible links between the Warmbad cluster and a series of kimberlite fields in Botswana (including Orapa) and possibly extending all the way to eastern Zambia near the southern end of the East African Rift which was suggested by Moore *et al.* (2008) to be a “megalineament” of alkaline activity as depicted in Figure 4.

### **3. The Chameis-Klinghardt-Gibeon lineament:**

The 30 to 75 Ma Chameis-Klinghardt-Gibeon lineament of southern Namibia (Verwoerd and de Beer, 2006). From southwest to northeast, it includes submarine alkaline volcanics dredged from Chameis

Bay off southernmost Namibia, the Dreyer Rucken and Schwarzenberg nephelinites near the coast (Moore, 1979; Spriggs, 1988), the Klinghardt phonolites (Marsh, 1987), the Tsirub nephelinites (Nakashole, 2007), the Dicker Willem carbonatite complex (Cooper and Reid, 1991), the Gibeon kimberlite province (Kurszlaukis *et al.*, 1998) and the nearby Gross Bruckaros carbonatite (Stachel *et al.*, 1994) as well as the Blue Hills ultramafic lamprophyres (Kurszlaukis *et al.*, 1999).

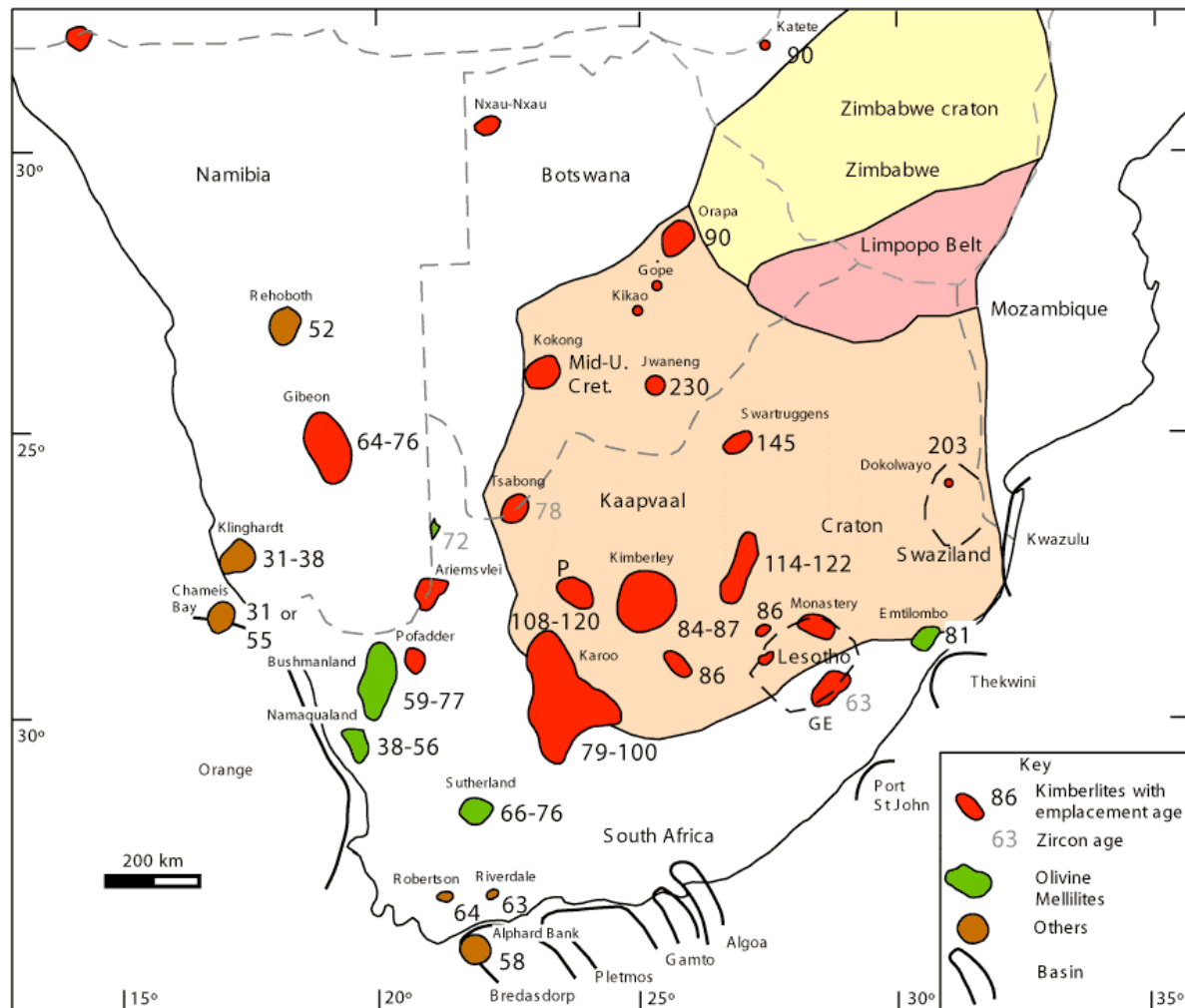


**Figure 4. Location and age ranges of southern African olivine melilitites, kimberlites and other alkaline rocks Modified after Moore *et al.* (2008).**

In addition to these lineaments, an occurrence of 6 olivine melilitite bodies occurs within the northern Kwazulu Natal Province near the town of Eshowe, on the east coast of South Africa (Colgan, 1992) (Figure 5). They were located as ilmenite anomalies during heavy-mineral loam sampling by De Beers from 1978 to 1980. A further four bodies showed up in the region but were not prospected. Their location and petrography were described in Colgan (1982) and was added in Colgan *et al.* (1989) as well as in an MSc thesis on their petrogenesis in Colgan (1992). These melilitites appear to be much older than, and unrelated to the melilitites along the western coast of southern Africa. However, they occur along the eastern continental margin and have similar ages to the kimberlite pipes found in Lesotho and Kimberly regions (Figure 4). Although there is no clear signs of age

progression with this cluster of olivine melilitites it is still of interest when considering the regional geology and main localities featuring olivine melilitites in southern Africa.

The much earlier Cambrian age Kuboos-Bremen Igneous Province located between the NBW lineament and the Chameis-Klinghardt-Gibeon lineament located near the Orange River in NW South Africa and southernmost Namibia is illustrated in Figure 4 (Smithies and Marsh, 1996). This alkaline magmatic lineament consists of a series of intrusive bodies made up of a range of alkaline rock types from the oldest south-western nepheline-bearing syenites to the youngest north-easterly granites as well as associated carbonatites and ultramafic lamprophyres (Smithies and Marsh, 1996). This is not Mesozoic-Cenozoic as with the other linear alkaline intrusives mentioned but its presence indicates a long-term pattern of related linear alkaline magmatism in this region.

### 2.3. Regional Geology:

The Namaqualand, Bushmanland and Warmbad magmatic clusters are mainly hosted by rocks of the Namaqua-Natal Mobile Belt, which is also called the Namaqua-Natal Province (NNP), that forms the largest Proterozoic mobile belt in South Africa (Eglington, 2006). The projected extent of this tectonic terrain is shown in Figure 5 (Verwoerd and de Beer, 2006; Moore, 1979).

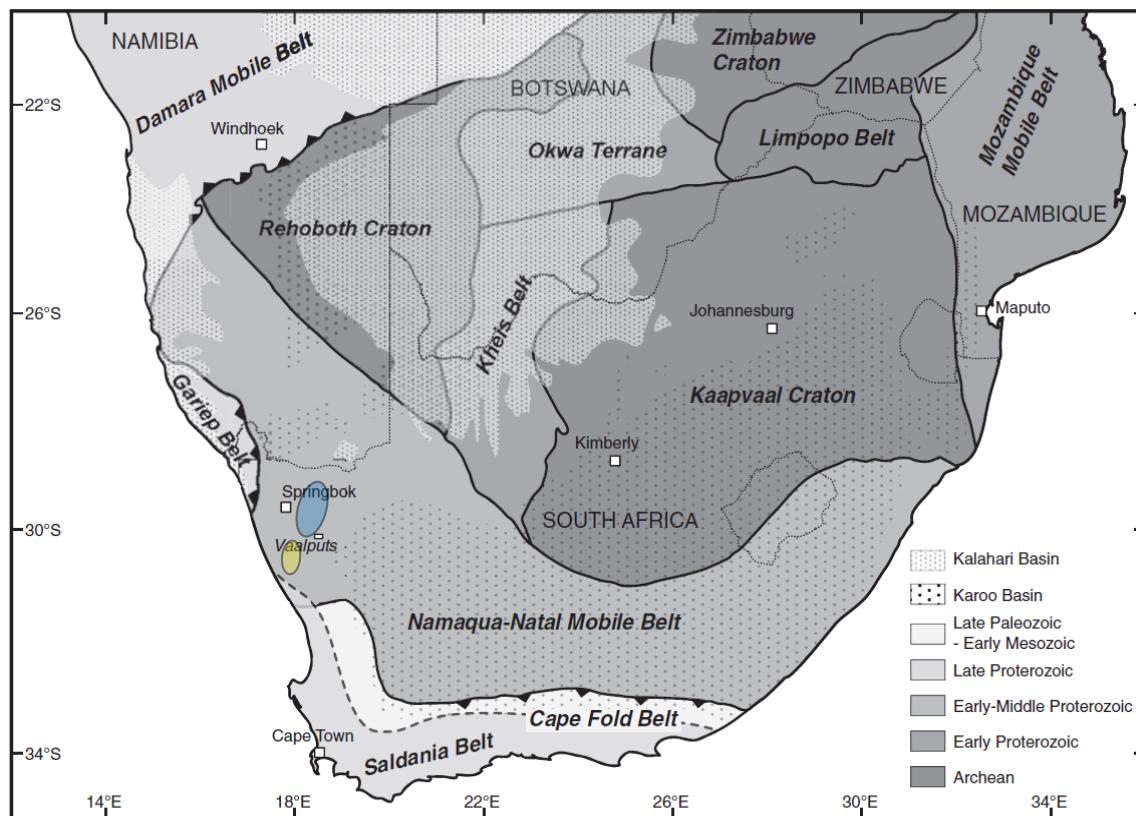


**Figure 5. Main tectonic elements of Southern Africa with the Namaqualand sampling area broadly highlighted in yellow and the Bushmanland area highlighted in blue (Modified after Viola *et al.*, 2012).**

The western margin of southern Africa consists of a large area of the Saldania Belt and Cape Fold belt extending to the south as well as the large area covered towards the interior by the Namaqua-Natal

Mobile Belt which is bordered by the Gariep belt and the Damara Mobile belt to the northwest, by the Rehoboth Craton to the north, the Kheis Belt to the northeast, the Kaapvaal Craton to the east as illustrated in Figure 5.

The basement rocks through which all Namaqualand and most Bushmanland melilitite pipes were emplaced fall within an area called the Garies Terrane (Figure 6) which forms the southern part of the Bushmanland Sub-province of the Namaqua-Natal Mobile Belt (Eglington, 2006; Cornell *et al.*, 2006). The Garies Terrane, together with the Aggeneys and Okiep Terranes makes up the Bushmanland sub-province of the Namaqua-Natal Mobile Belt (Hartnady *et al.*, 1985, Eglington, 2006). These terranes have all experienced several phases of deformation and metamorphism (peak metamorphism at 1.02 to 1.04 Ga) as well as mineralization in the Aggeneys and Okiep Terranes (Eglington, 2006; Cornell *et al.*, 2006).

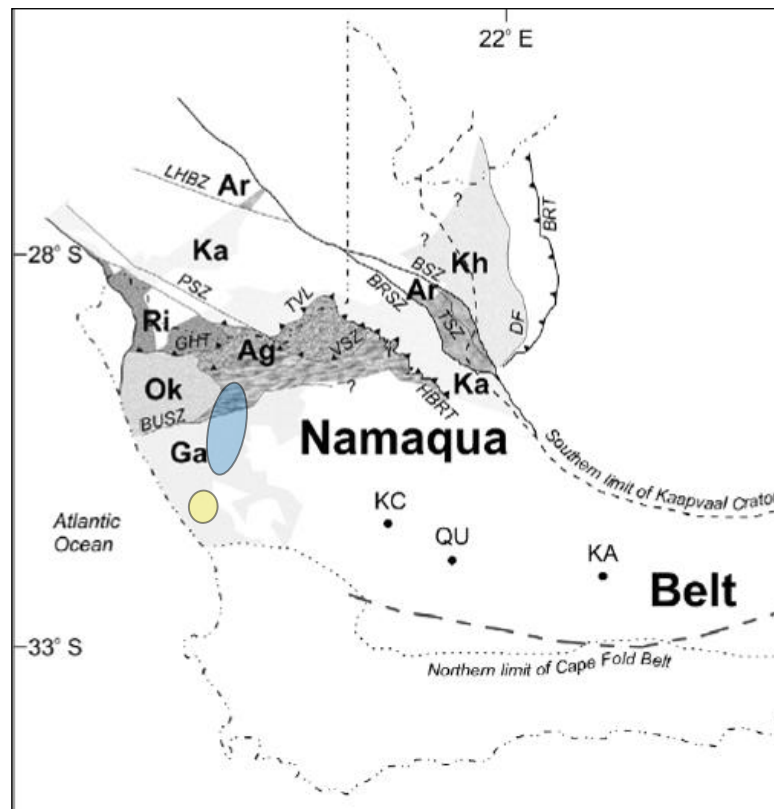


**Figure 6. Map showing the divisions of the Namaqua Mobile Belt into the regional tectonics zones. The Garies (Ga) Terrane and Aggeneys (Ag) Terrane are important regions for this study and are separated by the Buffels River Shear Zone. They both form part of the Bushmanland Sub-group within the Namaqua-Natal Supergroup (From Eglington, 2006). (Namaqualand sampling area broadly highlighted in yellow and the Bushmanland area highlighted in blue on the diagram).**

The Garies Terrane is the southernmost terrane and is separated from the Okiep Terrane and the Aggeneys Terrane to the north by the Buffel's River Shear Zone that becomes indistinguishable towards the west due to a younger sedimentary cover (Eglington, 2006). The Garies Terrain is dated at between 1.2 and 1.0 Ga based on zircon U-Pb ages from mainly metamorphic rocks, although many are metamorphosed granites (Eglington, 2006; Cornell *et al.*, 2006). The Garies Terrane consists of paragneisses and orthogneisses as well as voluminous granites and charnokites (Hartnady *et al.*, 1985;

Thomas *et al.*, 1996). Several phases of deformation are observed and the southern boundary of the Garies Terrane is unclear (Eglington, 2006; Cornell *et al.*, 2006). The main difference between the Garies Terrane and the northern Okiep and Aggeneys Terranes is that it shows little reworking of older protoliths while the northern terrains show significantly more (Eglington, 2006).

The southern part of the Bushmanland Cluster of olivine melilitite pipes also penetrates the Garies Terrane (Eglington, 2006). The pipes of the northern part of the Bushmanland Cluster are emplaced in basement rocks of the Aggeneys Terrane which consists of reworked Paleoproterozoic crustal rocks (Eglington, 2006). These consist mainly of para- and orthogneisses, metavolcanics and granites (Eglington, 2006). The Aggeneys Terrain has been dated to have formed between 1000 and 1200 Ma but also contains a significant population of older 1600 to 1700 Ma extrusive rocks (Eglington, 2006).

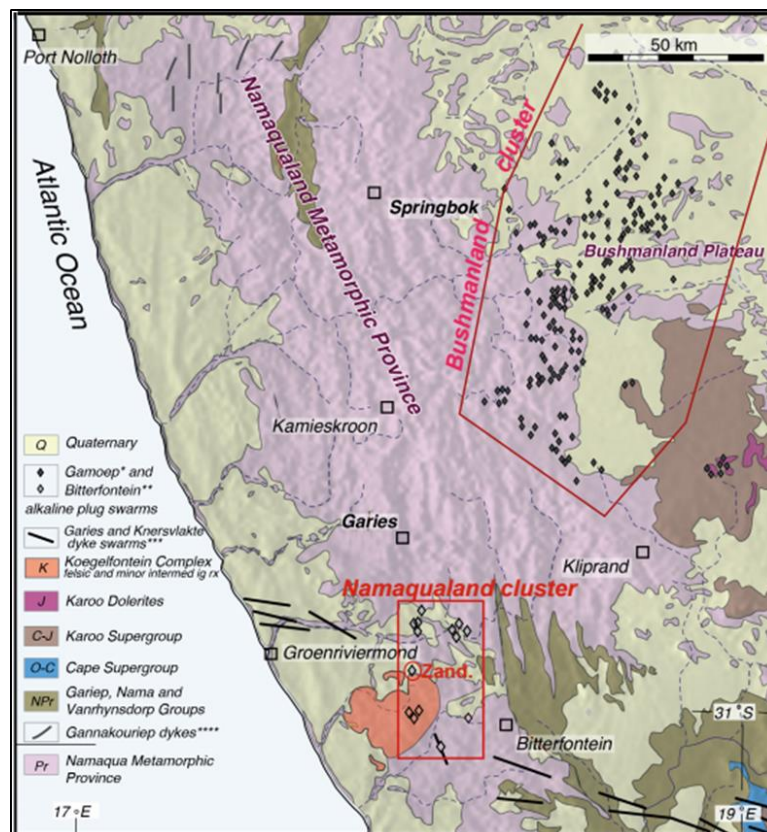


**Figure 7. Regional geology for the Namaqualand and Bushmanland clusters showing the approximate boundaries of the clusters as well as some of the pipes identified in each cluster shown as unfilled diamonds in Namaqualand and filled diamonds in Bushmanland. The original image was modified after Viola *et al.* (2012).**

The crustal thickness of the Namaqualand and Bushmanland area has been constrained using geophysical methods that show an approximate thickness of 38 to 48 km for the Namaqua-Natal Mobile Belt (Doucouré *et al.*, 1996; Priestly *et al.*, 2006; Janney *et al.*, 2010). From the coastal regions of South Africa towards the interior of the continent, a significant increase in thickness of the crust occurs such that the rocks of the lithospheric crust within the Namaqualand melilitite cluster would be significantly thinner than the more interior Bushmanland and Warmbad clusters (Doucouré *et al.*, 1996; James *et al.*, 2001; Globig *et al.*, 2016; Priestley *et al.*, 2008). This is enhanced by more erosion

along the coastal Namaqualand region while the Bushmanland region forms a higher topographic plateau with less erosion observed (Moore *et al.*, 2009; Viola *et al.*, 2012). The difference in lithospheric crustal thickness between the thinner coastal crust of Namaqualand versus the thicker crust in the Bushmanland region will be discussed later to understand how it may have influenced the petrogenesis of two seemingly related suits of magmatic rocks.

## 2.4. Local Geology:

The local geology reveals that in addition to the underlying Garies Terrane basement rocks of the Bushmanland Sub-group of the Namaqua-Natal Mobile Belt, the Namaqualand region contains sedimentary rocks of the Cape Supergroup and Gariep Supergroup to the east, as well as the overlying Karoo Supergroup rocks to the northeast (Figure 7). However, none of these are particularly relevant for this study because the Namaqualand pipes do not intrude through these sequences (Moore, 1979). Of significance for this study, as shown in Figure 7, are the Koegel Fontein Complex rocks and their associated metamorphic aureole as well as the more recent overlying Quaternary sediments see section 2.4.2 below (Viola *et al.*, 2012).

All of the Namaqualand olivine melilitite pipes are located within the Namaqua-Natal Mobile Belt, however, some of the pipes also intrude through the  $\approx 135$  Ma intrusive felsic alkaline granitic Koegel Fontein Igneous Complex, located roughly 30 km to the west of Bitterfontein (Verwoerd and de Beer, 2006). These include 5 pipes located on the farm Biesiesfontein which intrude into the Koegel Fontein Igneous Complex that will be described later (Moore and Verwoerd, 1985). The remaining pipes were emplaced through  $\approx 1.1$  Ga gneisses of the Garies Terrane.

The Namaqualand cluster has been illustrated in the map shown in Figure 8, which provides a simplified regional geological map of the Namaqualand pipes. The pipes are shown to intrude through the  $< 1170$  Ma Hunboom Gneiss, the  $< 1163$  Ma Meslip Gneiss and the Spektakel Suite of  $< 1090$  Ma granites which belong to the Namaqua-Natal Mobile Belt (Macey *et al.*, 2008).

The Zandkopsdrift Carbonatite and spatially related olivine melilitites are found exposed within areas partially covered by Quaternary sediments. The Waterval pipe is found in close proximity to the Hunboom Gneiss of  $< 1170$  Ma while the Dikdoorn and Dikdoorn Satellite pipes are found within the Meslip gneisses. The Louisfontein pipe towards the North East also occurs within the Meslip gneisses. The geological map (Figure 8) was created by simplifying and combining the local regional 250 000 geological maps of the Garies, Calvina and Louisfontein areas (i.e., Grobbelaar, 2010; de Beer, 2010; de Beer, 2000). Most of the Biesiesfontein pipes are believed to intrude through the Rietpoort granite of the Koegel Fontein Complex while two of these pipes (Biesiesfontein E and B) have also intruded through the overlying Spektakel Suite which forms a roof pendant over parts of the complex (Macey *et al.*, 2008).

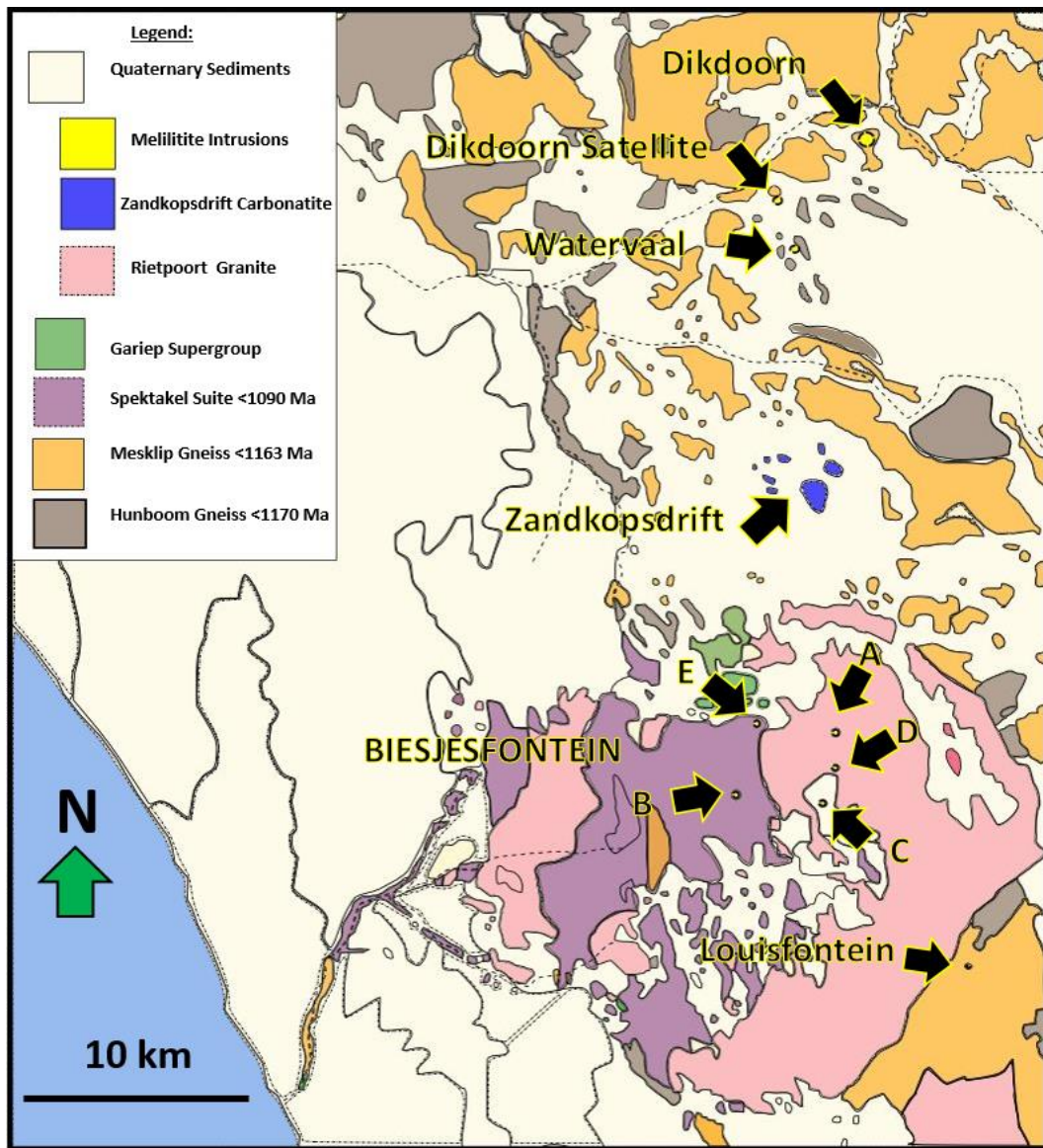


Figure 8: A simplified geological map of the Namaqualand region which shows the regional geology and the location of the pipes that were sampled. Compiled from the 1:250 000 geological maps from Loeriesfontein (Grobbelaar, 2010), Garies (de Beer, 2010) and Calvinia (de Beer, 2000).

#### 2.4.1 *Zandkopsdrift carbonatite and olivine melilitites:*

The Zandkopsdrift carbonatite complex is a 55 Ma igneous complex (Venter *et al.*, 2010) containing carbonatite breccia and dykes as well as aillikite (potassic ultramafic lamprophyre) and olivine melilitites (Ogunbuyi *et al.*, 2015). It is considered to be part of the Namaqualand cluster of the NBW lineament (Moore & Verwoerd, 1985). This intrusion of carbonatite and related magmas has likely been formed from a moderately fractionated carbonate-rich silicate parental magma (Ogunbuyi *et al.*, 2015). The Zandkopsdrift pipe is likened to a deeply weathered root zone of an intrusive carbonatite complex such as the Salpeterkop intrusion (Verwoerd *et al.*, 1995; Verwoerd and de Beer, 2006).

#### **2.4.2 *Koegel Fontein complex igneous rocks and their metamorphic aureole.***

The Koegel Fontein Complex is a dominantly felsic, anorogenic intrusive complex, dated 135 Ma (de Beer *et al.*, 2002) that can be seen as similar to the Damaraland intrusive complexes of north-western Namibia. The complex occurs near the towns of Kotzesrus and Bitterfontein and forms a roughly circular body consisting of two intrusive A-type granites namely the Rietpoort granite, Rooivleitijs granite as well as syenites, the Zout River mafic dyke as well as hypabyssal bostonites and quartz porphyries. Dolerite dykes related to the Atlantic Ocean opening are also present in the area (Verwoerd and de Beer, 2006; Curtis, 2010; Curtis *et al.*, 2013). The Koegel Fontein complex is one of the largest identified intrusive complexes that has been emplaced in the Cretaceous along the western coast of southern Africa and is very similar to the Damaraland intrusive complexes of north-western Namibia (Verwoerd and de Beer, 2006).

Prior to the breakup of Gondwana, in the Early Cretaceous, the well-known Parana-Etendeka Large Igneous Province of NE Brazil and NW Namibia were emplaced at  $\approx 135$  Ma (Peate, 1997). The Koegel Fontein complex is also considered to be part of the magmatism related to the breakup of Gondwana and rifting along the west coast during the separation of Africa and South America (Gerrard and Smith, 1982; Verwoerd and de Beer, 2006). There are also other alkaline intrusions along the West coast of Southern Africa (Harris, 1995; Trumbull *et al.*, 2004; Verwoerd and de Beer, 2006) that are considered to be related to Koegel Fontein complex which are the Damaraland intrusive complexes of northern Namibia (e.g., Okenyenya, Okorusu, Osongombo, Spitzkopppe, Brandberg, etc.) that are approximately the same age as the Parana-Etendeka large igneous complex in South America and Northern Namibia (Trumbull *et al.*, 2000; Trumbull *et al.*, 2004; Verwoerd and de Beer, 2006).

The Koegel Fontein complex intrusions are believed to be structurally controlled by areas of crustal weakness containing faults, associated fractures and shear zones related to the joining of two major faults which strike N-S and E-W (de Beer *et al.*, 2002). The Koegel Fontein region is also host to numerous quartz porphyry dykes that cut the basement rocks but not the Koegel Fontein complex suggesting that these dykes are older (Curtis *et al.*, 2013).

#### **2.4.3 *Low $\delta^{18}\text{O}$ for the Koegel Fontein complex.***

The Koegel Fontein Complex is notable for containing igneous rocks with the lowest  $\delta^{18}\text{O}$  values reported for igneous rocks in the southern hemisphere (Curtis, 2010; Curtis *et al.*, 2013). Some rocks from this complex extend to  $\delta^{18}\text{O}$  values as low as  $-4.1$  ‰. The presence of these extremely low  $\delta^{18}\text{O}$  signatures has been attributed to interaction with crustal rocks that had either experienced high-temperature hydrothermal alteration and/or had interacted with meteoric water during the Neoproterozoic Cryogenian (e.g., “Snowball Earth”) period (Curtis *et al.*, 2013).

It is important to note that these anomalous oxygen isotope values are only found in a small number of volumetrically minor dykes of the Koegel Fontein Complex (Curtis *et al.*, 2013). The volumetrically far more important Rietpoort and Rooivleitsjies granites have moderately heavy  $\delta^{18}\text{O}$  values typical of most granites in the Namaqualand region (Curtis, 2010; Curtis *et al.*, 2013). Similarly, the Damaraland intrusive complexes also have moderately heavy  $\delta^{18}\text{O}$  values and lack any indication of a low  $\delta^{18}\text{O}$  component (Harris, 1995; Trumbull *et al.*, 2004). Therefore, the negative normalized  $\delta^{18}\text{O}$  values are restricted to rocks formed from unique magmas that are likely to have interacted with crustal fluids.

This complex is important because it provides an opportunity to investigate the effect of anomalous crustal oxygen isotope compositions combined with those of olivine melilitites that are hosted within its domain, in order to determine if there is any influence on the  $\delta^{18}\text{O}$  values of the melilitites, and thereby assess the extent of crustal assimilation in the genesis of these magmas. This is important to understand as it allows us determine if the olivine melilite pipes have been significantly affected by crustal assimilation.

#### 2.4.4 ***Mafic dykes.***

The west coast of southern Africa from the Etendeka Province to the Cape Peninsula has numerous dyke swarms of early Cretaceous age which have been linked to the breakup of Gondwana (Trumbull *et al.*, 2007; Verwoerd and De Beer, 2006). Some of the dykes can be followed for tens of kilometres and vary between 1 to >20 m in length (Botha and Hodgson, 1976; Reid and Rex, 1994; de Beer *et al.*, 2002). The dykes are mostly sub-parallel to the coast, however, some strike in a NE-SW direction (Trumbull *et al.*, 2007). These dykes appear to be mainly tholeiitic, plagioclase-phyric basalts, with some mineralogical variations that suggest they may be Karoo age dolerite intrusions (Verwoerd and De Beer, 2006). The Koegel Fontein complex and Namaqualand/Bushmanland olivine melilitites are considered to be significantly younger than the large WNW striking dolerite dykes found along the west coast based on dating of the dykes at  $134 \pm 3$  Ma by Reid and Rex (1994). There is also a much older  $717 \pm 11$  Ma (Neoproterozoic age) dyke swarm in Namaqualand/Bushmanland region known as the Gannakouriep dyke swarm considered to have emplaced during the Pan African Gariep Orogeny/ Rodinia super-continental breakup (Reid *et al.*, 1991).

#### 2.4.5 ***Quaternary sediments.***

The regional basement rocks of the Namaqua-Natal Belt, the Koegel Fontein Complex and the Namaqualand and Bushmanland intrusive pipes are covered in areas by Kalahari age sediments, soil, calcrete and recent alluvial sediments which often limit their exposure at surface, however in some areas these pipes are still partially, to fully exposed (Verwoerd and de Beer, 2006; Viola *et al.*, 2012). The overlying quaternary sediments make the number of undiscovered pipes that exist in the region uncertain, especially as some pipes form low-lying erosional features or depressions that would likely

be hard to detect below sediments. Fortunately, due to early regional exploration for diamonds as explained by Cornelissen and Verwoerd (1975) the region has been relatively extensively explored for magmatic pipes exposed at surface because each pipe was considered to be a possible source for the west coastal diamonds and other local alluvial diamond deposits (Cornelissen and Verwoerd, 1975). The regional geological survey has also helped to establish the location of the pipes and locate any previously undiscovered pipes (de Beer, 2010). There likely exists a number of olivine melilitite pipes that have been eroded and covered by sediments which have not been exposed at surface (Viola *et al.*, 2012).

#### **2.4.6 *Non magmatic breccia filled pipes.***

The diatremes/pipes in the Namaqualand cluster have been eroded to a hypabyssal level of exposure, revealing a magmatic infilling, however, many of the pipes in the Bushmanland region show a lower level of erosion with a sedimentary infill exposed at the surface (More *et al.*, 2009). This has resulted in uncertainty as to the nature and composition of these pipes at depth. All the pipes in the Namaqualand and Bushmanland clusters are assumed to be magmatic at depth, however, some non-magmatic siliceous breccia-filled pipes are exposed at the surface in the region and therefore, may easily be confused with those related to alkaline igneous activity in the Namaqualand region (Svensen *et al.*, 2006; Olianti & Harris, 2018).

### **2.5. Description and formation of the pipes:**

In the Namaqualand and Bushmanland region, three main types of pipes are seen at the surface which are: (1) Sediment-filled pipes, (2) volcanoclastic breccia-filled pipes and (3) magma-filled pipes (Cornelissen and Verwoerd, 1975). While the sediment-filled pipes have less significance for this study, it is assumed that all these are magmatic in origin and igneous rock pipes in which magma exists at depth. The magma-filled pipes are the focus of this study as they generally have preserved areas of relatively fresh igneous rock.

The formation of the Namaqualand and Bushmanland pipes is considered to be similar to that of kimberlite pipes which also erupt from great depth as explosive, CO<sub>2</sub>-rich ultramafic magmas (Moore, 1979; Cornelissen and Verwoerd, 1975). However, olivine melilitites are often preserved with an elevated topography due to their mineralogy and fine-grained texture and resistance to weathering compared to kimberlite, which results in their preservation when compared to most of the surrounding country rock types (Cornelissen and Verwoerd, 1975, Moore & Verwoerd, 1985, Moore, 1979). They are believed to have erupted as magmatic diatremes (Moore, 1979) which are funnel or cone-shaped bodies with steep sides (Sparks *et al.*, 2006). It is assumed that these magma-filled pipes extended to the surface where tuff rings of excavated volcanoclastic debris as per the model first suggested by Cloos (1941). Closer to the surface the pipes are filled with brecciated country rock mixed with magmatic material (Mitchell, 1997, Sparks *et al.*, 2006). Due to post-eruption gradual sedimentary

infilling, these pipes often contain a polymictic basal sedimentary breccia that fines upwards towards coarse sands, silts and clays as illustrated in Figure 9 (Cloos, 1941; Mitchell, 1997; Sparks *et al.*, 2006; Cornelissen and Verwoerd, 1975).

### **1. Sediment-filled pipes:**

Sediment-filled pipes have only been identified in the Bushmanland region where they typically occur as large shallow depressions of sometimes ~2 m below ground surface with a sequence of sediments that have filled the pipes without evidence of any igneous rocks or volcanic breccia exposed at the surface as with the schematic example provided in Figure 9 (Moore, 1979; Visser *et al.*, 1984). These pipes often contain finely bedded volcanoclastic or locally derived sediments which were deposited during and after the pipe formation (Cornelissen and Verwoerd, 1975). Many of these sediment-filled pipes contain fossils or sediments that no longer exist in the surrounding areas around the pipes due to their age and the level of erosion that has occurred (Verwoerd and De Beer, 2006; Visser *et al.*, 1984; Cornelissen and Verwoerd, 1975).

### **2. Volcaniclastic-breccia-filled pipes:**

The volcaniclastic breccia-filled pipes are most prominent in the Bushmanland area and are filled with magma and rock breccia derived from local upper crustal sedimentary granitic and metamorphic rocks (Cornelissen and Verwoerd, 1975; Visser *et al.*, 1984). These volcaniclastic breccia-filled pipes vary in size from ~50 to ~500 m in diameter and vary with grain size and sorting from very coarse angular poorly sorted material to fine-grained layered material, suggesting violent as well as more tranquil episodes of crater infilling (Cornelissen and Verwoerd, 1975). The upper few meters of these pipes have in many cases been mineralised by meteoric fluids and are now a dark brown to dark red-orange colour. The cap zones of these breccia-filled pipes often contain high concentrations (up to many thousands of ppm) of rare earth elements and other rare metals such as Ba, Nb, U and Th (Marageni & Janney, 2018). In terms of their outcrop pattern, these pipes often resemble kimberlites and several of them have yielded kimberlite indicator minerals such as garnet and ilmenite with compositions indicative of an origin from fertile (and non-diamondiferous) mantle sources (P.E. Janney, personal communication, 2015). While many of the altered, volcaniclastic breccia-filled pipes in the Bushmanland cluster have historically been identified as kimberlite pipes (Cornelissen and Verwoerd, 1973), these do not meet the volcanological or petrographic criteria to be correctly classified as kimberlites.

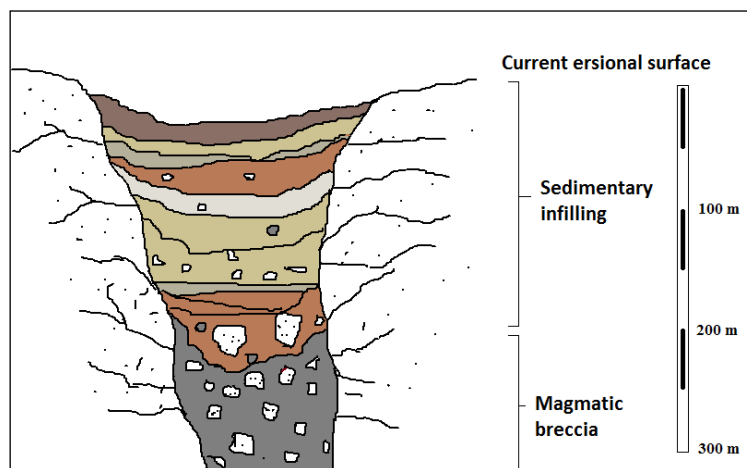


**Figure 9. Geological cross-section extrapolated for the Koppieskraal pipe K5 from the Bushmanland cluster based on the prospector's core drilling which revealed an altered magmatic breccia below a sedimentary infilling. Modified after Cornelissen and Verwoerd (1975).**

### 3. Magmatic pipes:

The magmatic pipes are typically composed of olivine melilitite or closely related rock types such as olivine nephelinites and nephelinites (Moore, 1979, Visser *et al.*, 1984; Visser, 1989). For this study, these magmatic varieties, namely olivine melilitites, olivine nephelinites and nephelinites, have been collectively called “melilitites” and will thus be called the Namaqualand or Bushmanland “melilitites” for simplicity. These pipes have been eroded to form low hills or, more rarely, flat areas or depressions which vary in size from ~40 to ~400 m in diameter (Cornelissen and Verwoerd, 1975; Moore, 1979; Visser *et al.*, 1984). Therefore, two morphologies of magmatic pipes are found: A) Rubble-strewn hills/mounds (Figure 10A) and B) low-elevation pipes forming flat areas or depressions covered by boulders and soil (Figure 10B).

A). The rubble-strewn hills/mounds are melilitite pipes that pipes often form distinct dark brown coloured, rubble-strewn hills which are often distinguishable from surrounding hills by their uniform rounded nature and darker colour (Cornelissen and Verwoerd, 1975). The hills of weathered rock often contain boulders of both weathered and also relatively fresh rock and a dark reddish-brown soil (Cornelissen and Verwoerd, 1975). Most of the material found are small boulders with a weathered outer layer and cores of relatively fresh material (Moore, 1979).

B). The melilitite pipes that form flat areas encompassing shallow depressions are found in both the Bushmanland and Namaqualand clusters (Moore, 1979; Verwoerd and De Beer, 2006) and appear to have preferentially weathered in comparison to the surrounding country rocks to form flat areas or pans with scattered boulders and fragments of melilitite (Cornelissen and Verwoerd, 1975; Moore, 1979; Visser *et al.*, 1984). Cornelissen and Verwoerd (1975) note that in calcrete and sand-covered plateaus, the pipes are usually covered by soil and calcrete that results in poor exposure, making them almost indistinguishable from the sediment- or breccia-filled pipes at the surface except for slightly darker soil (Moore, 1979; Visser *et al.*, 1984). Figure 10B provides an example of a pipe that has a flat eroded surface with a similar elevation to the surrounding country rock.

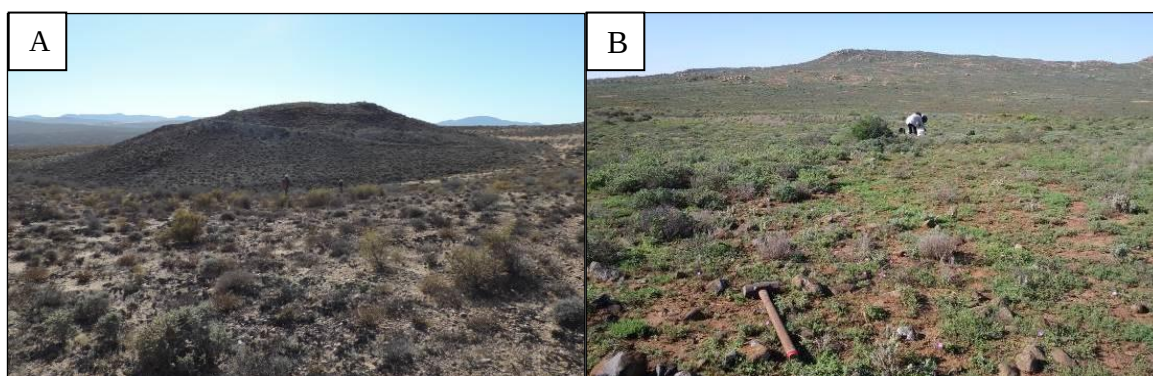


**Figure 10. A). An east-facing view of the Dikdoorn pipe in Namaqualand which forms a rubble-strewn hill with gentle slopes covered in small boulders of melilitite. B). The Biesiesfontein pipe E pipe that forms a shallow depression with poor exposure with a few boulders at surface and pipe boundaries covered by sediments.**

## **2.6. Magmatic rock types identified within the Namaqualand cluster.**

The rock types that have historically been identified in the Namaqualand and Bushmanland clusters are briefly described to provide an overview of what has been described. These rock types typically all contain olivine, titanomagnetite and perovskite. The five rock types were found in the Namaqualand pipes which are (1) olivine melilitites, (2) nephelinites, (3) olivine nephelinites (4) vesicular olivine melilitites and (5) pegmatitic melilitites.

### **1. Olivine melilitites:**

Olivine melilitites are a relatively commonly found rock type in the Namaqualand region. Olivine melilitites by definition have >10% olivine and >10% melilite, and they commonly have a very fine-grained (less than 0.2 mm diameter grains) to fine-grained (0.2-0.5 mm) groundmass of variable composition (Moore, 1979). They have been described as porphyritic rocks with phenocrysts of olivine and lesser ilmenite as well as microphenocrysts of titanomagnetite and perovskite in a matrix consisting of variable amounts of melilitite, phlogopite, clinopyroxene, serpentine, calcite, apatite, melilite, garnet, nepheline, monticellite, perovskite and spinel (Moore, 1979; Verwoerd and de Beer, 2006). Euhedral to subhedral titanomagnetite and perovskite microphenocrysts are present in nearly all the olivine melilitites with a groundmass that may contain clinopyroxene needles, interstitial nepheline, fine granular titanomagnetite and melilitite laths (Verwoerd and De Beer, 2006). When compared to the Bushmanland olivine melilitites, the Namaqualand olivine melilitites have a lower modal abundance of olivine phenocrysts overall but are otherwise indistinguishable (Moore, 1979).

### **2. Olivine nephelinites:**

The olivine nephelinites contain modal clinopyroxene of >10 % and a low content of melilite (less than 10 %) which is generally absent or partially replaced by clinopyroxene in these samples (Moore, 1979; Verwoerd and de Beer, 2006). In the coarser-grained varieties, the matrix contains an interlocking network of euhedral to subhedral clinopyroxene needles, intergrown with titanomagnetite

and perovskite microphenocrysts, as well as, interstitial nepheline that represents >10% of the sample. The much finer-grained varieties of olivine nephelinites become nearly indistinguishable from fine-grained olivine melilitites, however in these samples, the absence of melilite phenocrysts is the main difference used to define them as nephelinites as per the definitions by Moore (1979).

### **3. Nephelinites:**

Modally, these rocks are similar to olivine nephelinites, however, they contain less than 10% olivine (Moore, 1979). These rocks mainly contain a variable groundmass grain size from medium to fine-grained. Rocks with a fine-grained indistinguishable fine crystalline matrix and a very low content of melilite and clinopyroxene could also be defined as by the broader term olivine-bearing ultramafic volcanics.

### **4. Vesicular and brecciated melilitite pipes:**

Within the Namaqualand and Bushmanland area, melilitite pipes with a vesicular magmatic texture may contain country rock xenoliths and xenocrysts (Verwoerd and De Beer, 2006; Moore, 1979). In some cases, the vesicles are filled with calcite to form an amygdaloidal texture. This type of vesicle-rich melilitite may be found as isolated boulders or as isolated exposures (Moore and Verwoerd, 1985, Moore, 1979). Due to poor surface exposure, in many of the pipes, the vesicular melilitite is likely to be under-represented by exposure and sampling due to the relatively more rapid weathering of this rock type (Moore, 1979). In most cases, the olivine melilitite pipes from the Namaqualand region are poorly exposed, with few lithological contacts and structural features visible. However, some of these pipes, most notably the pipes called Dikdoorn by Moore (1979) and the Biesiesfontein pipe D are fairly well exposed and display an equant outcrop pattern, with an outer vesicular margin and a vesicle-free interior.

### **5. Pegmatitic melilitites pipes:**

In both clusters, a melilitite rock type is also found with an unusually coarse, pegmatoidal grain size (Verwoerd and De Beer, 2006). The pegmatoidal samples contain predominantly clinopyroxene, titanomagnetite, olivine and nepheline with accessory perovskite and phlogopite (Moore and Verwoerd, 1985; Verwoerd and De Beer, 2006). Melilite is generally absent in the coarser-grained lithologies mentioned (Verwoerd and De Beer, 2006). Moore (1979) estimates the pegmatitic type olivine melilitites to account for less than 1% of the volume of the pipes in which they are found.

## **2.6.1 Mineralogical Characteristics of the pipes:**

The mineralogical characteristics of the pipes previously studied showed that olivine is present in most of the pipes as a major to dominant phase present as phenocrysts with a size range between 3 and 1 mm as fine-grained fragments. A range of groundmass mineral coarseness was observed in the olivine melilitites and olivine nephelinites studied by Moore (1979) which varied from coarse to fine-

grained. The very fine-grained specimens may or may not contain fine-grained clinopyroxene phenocrysts (<0.02 mm diameter) as well as microphenocrysts of perovskite, titanomagnetite and a very fine-grained glass forming a dense mat. However, nepheline and glass are difficult to distinguish in these fine-grained samples and phlogopite has not been observed (Moore, 1979). The coarse- to medium-grained samples of olivine melilitite have larger grains of melilite, titanomagnetite, perovskite and interstitial nepheline (Moore, 1979).

In most of the samples, titanomagnetite is present as a common phase and shows a continuous size range down from <1 mm to groundmass dusting size grains in most of the samples (Moore, 1979). However, in some samples, up to 10 mm diameter titanomagnetite anheda are found (Moore, 1979). Perovskite is present as a ubiquitous microphenocrystic phase that forms anheda and cubes (Moore, 1979).

Melilite is abundant in some samples and absent in others (Moore, 1979). The melilite-bearing samples are often mineralogically similar to the rocks without this mineral. However, the samples with a coarser-grained groundmass are generally melilite-free. Moore (1979) distinguishes these melilite-free samples from olivine melilitites and names them olivine nephelinites as the term melilitite cannot be used if melilite is absent or below 10 % as previously stipulated by IUGS.

Minor amounts of clinopyroxene can be observed in some of the olivine melilitite samples while it is absent in others (Moore, 1979). The coarser-grained olivine nephelinites have an interlocking groundmass of medium (0.5 mm length) to coarse (1 to 2 mm length) elongate clinopyroxene laths which are found with titanomagnetite, perovskite and interstitial nepheline (Moore, 1979).

Phlogopite is found as an interstitial phase in the coarser-grained olivine nephelinite samples and apatite has also been observed in the coarser samples (Moore, 1979). Some of the samples contain rare picroilmenite grains with a rim of skeletal titanomagnetite and outer fingers of perovskite (Haggerty *et al.*, 1985). A sulphide phase (likely to be pyrite) is observed in reflected light and occurs as disseminated angular to cubic grains in trace amounts (Moore, 1979).

The Namaqualand olivine melilitite pipes are generally free of mantle and crustal-derived xenoliths and megacrysts, while the Bushmanland pipes may contain mantle-derived megacrysts of olivine, ilmenite and xenoliths of mantle and crustal origin (Moore, 1981).

### **2.6.2 *Areas of post-emplacement alteration and calcritization:***

After the emplacement of the pipes, it appears that weathering, alteration and calcretization have affected areas of the Namaqualand and Bushmanland pipes making portions of them different to their original composition. Viola *et al.* (2012) describes the weathering profiles and calcritization parts of the Bushmanland and Namaqualand region which explains how the pipes and surrounding rocks were affected. Moore (1979) suggests that some of the pipes may form conduits for hydrothermal and meteoric fluids which resulted in pervasive post-emplacement alteration of portions of some of the pipes. The pipes where this has occurred are typically not well exposed and contain proportions of

fresh and portions of altered igneous rocks due to the action of deuteric, hydrothermal or meteoric fluids as well as surface weathering (Cornelissen and Verwoerd, 1975). During this study, care was taken to select samples that show the least evidence of post-emplacement alteration. Therefore, for the samples collected, post-emplacement alteration effects are relatively minimal.

## **2.7. Conditions for the formation of olivine melilitites:**

Olivine melilitites and nephelinites are considered to be a rare magma type (Brey, 1978) that generally occur in three main tectonic settings, including mature oceanic islands (Clague and Frey, 1982), continental rifts (Wilson *et al.*, 1995), and within stable continental settings (Brey, 1978, Day *et al.*, 2014). Olivine melilitites are often found in the vicinity of other alkaline rocks such as lamprophyres and carbonatites or are associated along magmatic lineaments with kimberlites (Wilson *et al.*, 1995; Dalton and Presnall, 1998). It is rare for kimberlites and melilitites to be found together in the same magmatic cluster, which can be explained by the occurrence of kimberlite magmas forming in thicker lithosphere than for melilitites (Mitchell, 1997; Winter, 2001). The location of olivine melilitites preferentially on thickened oceanic or intermediate-thickness off-craton continental lithosphere seems to be determined by the relatively restricted pressure and temperature conditions required for their formation (Brey, 1978).

Experimental studies have improved our understanding of the specific temperatures, pressures and source lithologies required for the generation of different mafic alkaline magma types (Girnis *et al.*, 2013; Dasgupta *et al.*, 2009; Keshav *et al.*, 2005; Dasgupta and Hirshmann, 2010; Pilet, 2015; Dalton and Presnall 1998; Moore and Wood, 1998; Mitchell and Tappe, 2010). Certain conditions for the formation of olivine melilitites have been proposed based on the results of experimental melting studies at high temperatures and pressures when considering the formation of deep mantle-derived rocks (Brey and Green, 1977; Brey, 1978). The general major and trace element geochemistry of olivine melilitites suggests they are derived from a low degree of partial melting (<5-1%) of an incompatible element-enriched, carbonate- and phlogopite bearing garnet peridotite from pressures between 40 to 30 kb (3 GPa) (Eggler *et al.*, 1988; Rogers *et al.*, 1992; Brey 1978). Specifically, Brey (1978) found that the relatively SiO<sub>2</sub> undersaturated olivine melilitite compositions such as those in South Africa, could originate from depths of  $\approx 35$  k-bars or  $\approx 105$  km depth at 1120-1180 °C from carbonate-bearing pyrolite (i.e., fertile peridotite) mantle sources by lower degrees of partial melting than that responsible for the generation of the less silica undersaturated olivine melilitites found elsewhere (e.g., the Rhine Graben and Tasmania; Brey, 1978).

There are a number of possible sequences of events in the mantle to explain the formation of low Si alkali magmas based on high-pressure experiments and thermodynamic constraints which is discussed by Pilet (2015). One model suggests that these magmas from the melting of pyroxenites derived from ocean crust, however, it appears that the major and trace-element characteristics of the magmas cannot easily be explained by this model. Therefore a modified scenario is favoured

involving metasomatism (Pilet, 2015). The three possibilities suggested involving recycled ocean crust which can explain the enriched isotopic signatures present in these melts which are:

1. Melting of ocean crust by the thermal upwelling of peridotitic mantle to produce a metasomatized peridotite which further melts due to elevated CO<sub>2</sub> to produce alkaline magmas (Pilet, 2015).
2. Melting of peridotite in the presence of CO<sub>2</sub> could result in magma that may mix with a melt derived from ocean crust to produce a trace-element enriched signature (Pilet, 2015).
3. A heterogeneous asthenosphere mantle melts to produce an isotopically variable composition that metasomatizes the lithosphere with veins of an isotopically enriched composition which accumulate and ultimately this enriched lithosphere melts again to produce the isotopically enriched melts that reach the surface (Pilet *et al.*, 2011).

Dasgupta and Hirshmann (2010) suggest two sources for the carbonate that can drive melting. One possibility is the outgassing of areas of the carbonated mantle which melt due to decompression melting in areas of uplift and rifting. The other source is carbonate resulting from degassing of subducted oceanic lithosphere (Dasgupta and Hirshmann, 2010). This is likely to explain the association between isotopically enriched alkaline magmas like the Namaqualand melilitites and carbonate melts such as the Zandkopsdrift carbonatite found in the same magmatic (Dasgupta and Hirshmann, 2010).

## **2.8. Oxygen isotopes within the Namaqualand melilitites:**

From the available literature, it is evident that there have been no reported oxygen isotopes measurements for the Namaqualand melilitite pipes. However, the pioneering work of Day *et al.* (2014) who revealed the first oxygen isotope variations in other South African olivine melilitites served as a motivation to continue the testing of oxygen isotopes in the Namaqualand olivine melilitites in this study.

The work of Day *et al.* (2014) focused on the measurement of whole rock samples and single olivine crystals. Their study aimed to compare oxygen isotope data from South African olivine melilitites with existing data from continental lithospheric mantle peridotites and OIB with and without HIMU signatures to help understand the origin of the South African olivine melilitites (Day *et al.*, 2014). They found that the olivines from these olivine melilitites have oxygen isotope values of between 4.99-5.26‰ with an average value of  $5.14 \pm 0.17$ ‰ which is within the range of mantle-derived olivines as suggested by Matthey *et al.* (1994). The results of their study led to the conclusion that this limited selection of South African olivine melilitites studied requires a source with oxygen isotope characteristics of peridotitic mantle as well as a HIMU-like mantle source based on radiogenic isotope ratios studied.

For the unfamiliar reader, there are three stable oxygen isotopes which are <sup>16</sup>O, <sup>17</sup>O and <sup>18</sup>O, of which only two (<sup>18</sup>O and <sup>16</sup>O) are commonly measured and reported in geochemistry. The <sup>18</sup>O/<sup>16</sup>O ratio of an oxygen-bearing substance is of interest because it may be fractionated by equilibrium

fractionation or physical-chemical fractionation (Freidman and O'Neil, 1977; Sheppard *et al.*, 1986, Day, 2004) which can result in differences in the oxygen isotope ratio in rocks. Fractionation occurs due to the mass differences between oxygen isotopes, which can cause significant variations in the isotope ratio of co-existing phases at equilibrium. This is significant for oxygen isotopes analysis because the isotopic fractionation of light elements like oxygen is more prevalent, whereas mass-dependent fractionation of heavier elements such as Sr, Nd, Hf, Os and Pb is generally not as prevalent (e.g., Day, 2004).

Because the ratios of heavy to light isotope are small and the natural variation is not that large, stable isotope are traditionally expressed using delta ( $\delta$ ) notation in units of per mil (‰).  $\delta^{18}\text{O}$  or delta-O-18 is a measure of the ratio of stable isotopes oxygen-18 ( $^{18}\text{O}$ ) and oxygen-16 ( $^{16}\text{O}$ ).  $\delta^{18}\text{O}$  is calculated using the following equation:

$$\delta^{18}\text{O} = \left[ \left( \frac{^{18}\text{O}/^{16}\text{O}}{(^{18}\text{O}/^{16}\text{O})_r} \right) - 1 \right] \times 1000 \quad (1)$$

s=sample

r=reference: standard mean ocean water (SMOW)

Therefore, if  $\delta^{18}\text{O} > 0$ , then the sample has a higher  $^{18}\text{O}/^{16}\text{O}$  than seawater and if  $\delta^{18}\text{O} < 0$ , then the sample has a lower  $^{18}\text{O}/^{16}\text{O}$  than seawater. (Kendal and Caldwell, 1998). The use of oxygen isotopes to discriminate between mantle sources that contain recycled lithosphere has been possible in some cases because the  $^{16}\text{O}/^{18}\text{O}$  isotopes can be strongly fractionated at Earth's surface by low and high-temperature processes that take place in the upper oceanic sediment and crust (Freidman and O'Neil, 1977).

The main cause of the change in  $\delta^{18}\text{O}$  in mantle-derived igneous rocks in oceanic settings is the isotopic difference between seawater and mid-ocean ridge basalt (MORB) which results in an interaction where the  $\delta^{18}\text{O}$  of the rock is changed due to rock-water O-isotope fractionation which is higher at low T and approaches zero at 800°C (high T) resulting in higher  $\delta^{18}\text{O}$  values at low temperature and lower  $\delta^{18}\text{O}$  values at high temperature (Freidman and O'Neil, 1977). However, the fractionation of light elements like oxygen tends to be much greater at low-temperature than at high, i.e., magmatic, temperatures (Freidman and O'Neil, 1977; Sheppard *et al.*, 1986, Day, 2004).

While most crustal rocks will have higher  $\delta^{18}\text{O}$  than mantle values, low  $\delta^{18}\text{O}$  values can be formed in both oceanic crust and continental crust. Therefore, Balsley and Gregory (1998) confirm that low  $\delta^{18}\text{O}$  magmas are believed to be formed by the melting of rocks that are formed by intense hydrothermal alteration by meteoric water. However, low  $\delta^{18}\text{O}$  magmas are unusual worldwide with some low  $\delta^{18}\text{O}$  magmas being found in Yellowstone and Iceland (Balsley and Gregory, 1998). Such low  $\delta^{18}\text{O}$  magmas are considered to be the main source from which low  $\delta^{18}\text{O}$  crystals are believed to form as the fractionation of oxygen isotopes during crystallization only has a limited effect (Balsley and Gregory, 1998).

The abundance of oxygen does not vary significantly between the mantle and crustal reservoirs, meaning that the  $^{18}\text{O}/^{16}\text{O}$  ratios of mantle-derived igneous rocks should vary linearly with the proportion of isotopically distinct crustal material assimilated into mantle sources, provided the

sample has not experienced significant alteration (Day, 2004; Day *et al.*, 2014). For this reason, oxygen isotopes can be extremely useful to indicate where the assimilation of altered crustal or mantle material has occurred within the igneous rocks (e.g., Bindeman, 2008). The situation is more complicated for mantle-derived igneous rocks in continental settings as even with the use of oxygen isotopes it is difficult to easily distinguish between examples of the incorporation of deeply recycled sedimentary (crustal) material and the shallow assimilation of continental crust by a magma (Day, 2004; Day *et al.*, 2014). Magmas which have assimilated material with a lower  $\delta^{18}\text{O}$  would crystallize into a rock that reflects a corresponding lower  $\delta^{18}\text{O}$  whole rock composition and thus minerals crystallizing from this magma would reflect a similar lower  $\delta^{18}\text{O}$  inherited from the magma with a lower  $\delta^{18}\text{O}$ .

The O-isotope ratio value of peridotitic mantle is considered to be relatively homogeneous ( $\delta^{18}\text{O} = 5.18 \pm 0.28$ ; Matthey *et al.*, 1994) which allows for O-isotopes to be used to identify mantle-derived magmas that have been contaminated by crustal material (either from local assimilation or incorporation of deeply recycled components; e.g., Eiler *et al.*, 2000; Eiler, 2001, Day *et al.*, 2014). Mantle that contains lithologies such as eclogite and pyroxenite derived from the oceanic crust will likely be more variable in composition than peridotitic mantle (e.g., Eiler *et al.*, 2000; Eiler, 2001). The  $^{18}\text{O}/^{16}\text{O}$  ratio of a source-rock is only minimally affected by ageing in the mantle or by metamorphic or magmatic processes at high temperatures (Taylor, 1968; Eiler, 2001) such that these factors are unlikely to explain the ratios present.

### 2.8.1 ***Rationale for single crystal olivine oxygen isotope analysis:***

Olivine is typically the earliest crystallizing mineral, therefore, understanding its oxygen isotope characteristics provides an important constraint on the magma's initial composition (and that of its source) as well as the degree of crustal contamination it may have experienced. For this study, oxygen isotope data is measured from the analysis of olivine crystals, while whole-rock oxygen isotope compositions were not measured due to the possible effects of low-temperature alteration on some of the samples and the potential presence of crustal xenoliths and xenocrysts in these rocks, which could affect the whole rock oxygen isotope compositions (Bindeman, 2008).

Instead of whole-rock analysis, the olivine phenocrysts were analysed by laser fluorination to determine the variation in oxygen isotopes. Oxygen isotope analysis was traditionally done on whole rock powders (Bindeman, 2008). However, the precise analysis of Mg-rich olivine, made possible by the development of the laser fluorination technique (Sharp, 1990), provides oxygen isotope data that are more reliably free of the effects of near-surface, post-emplacement alteration, since alteration of olivine separates is easily recognised and avoided (e.g., Harris *et al.*, 2015). The measurement of oxygen isotopes during this study will be described in more detail in the methodology that follows.

### **3. METHODOLOGY:**

#### **3.1. Locality Selection.**

Pipes for sample collection were identified and selected from geological maps and co-ordinates from Moore (1979) and Moore and Verwoerd (1985) as well as Google Earth and the 1:250 000 geological maps compiled by the Council for Geosciences from Loeriesfontein (Grobelaar, 2010), Garies (de Beer, 2010) and Calvinia (de Beer, 2000). The locations from previous studies were used to help identify the locations of the pipes on Google Earth satellite images. From the Google Earth satellite images and GPS coordinates, farm boundaries, roads and farm locations obtained from local toposheets were used to navigate to the sites where pipes are exposed. Other pipes such as Louisfontein were found solely using Google Earth. Some of the pipes noted on the Garies, Calvinia and older Bitterfontein maps were searched for in the field but not found suggesting that they have a very low surface exposure or had been extensively weathered. In aerial photography and satellite images, it is often unclear what the exact shape of the pipes is due to poor exposure and eroded contacts with country rock (Cornelissen and Verwoerd, 1975; Moore, 1979). Identification of some pipes is made harder due to the presence of 1-2 m thick calcrete coverings on their surfaces (Cornelissen and Verwoerd, 1975).

#### **3.2. Sample Collection.**

Field work for this project was done in three trips which were in June 2013, March 2014 and July 2015. During these trips, a collection of 45 samples were collected from 9 olivine melilitite pipes in the Namaqualand region. The DIK-10, samples were collected in the 1970s by geologists within the University of Cape Town and were included in this study as they are fresh and their location is known. The sample names and their locations are recorded in Appendix A where the GPS coordinates are also provided with the location of the samples and their respective pipe names. The country rock samples collected from exposures near some of the pipes were also sampled, described and analysed with the intention of characterizing the crustal rocks into which the olivine melilitites intruded. Unfortunately, no metamorphic or alteration aureole was found around any of the pipes due to poor exposure at the contacts of the pipes.

Once a pipe was located, the first step was to determine the extent of exposure and areas of the outcrop. If an outcrop was located, these areas were sampled by taking one sample per location. More than one sample was selected if the material seemed inhomogeneous. For some of the pipes (e.g., BIES pipes B and C) the only material available was surficial rubble. A GPS measurement was taken for the location of each pipe so that it could be located on a map for future reference.

Rock samples were split open on-site to determine the degree of weathering within the sample interior and where possible, large (> 5 kg) fresh samples were selected for this project. The focus of

this study is on fresh material to obtain the highest quality geochemical and petrographic data which is representative of the original magma. However, in the case of two pipes, Dikdoorn and Biesiesfontein pipe A, moderately altered, vesicular melilitite from the outer zones of the pipes was also sampled and analysed in addition to non-vesicular hypabyssal melilitite from the centre of the pipe. This was done because these pipes are two of the larger, better-exposed pipes and these samples could provide useful information on the structure and development of these pipes.

### 3.3. Sampling Localities.

The details of the localities visited during this study are shown in Figure 11 and summarized in Table 1 as well as listed in Appendix A Table 18 which provides GPS coordinates for each sample. The map shown in Figure 11 clearly shows a spatial difference between the northernmost pipes in the Namaqualand cluster [i.e., Dikdoorn (DIK), Dikdoorn Satellite (DSAT), and Waterval(WAT)] and the southernmost pipes on the farms Biesiesfontein and Louisfontein [BIES A, B, C, D and E as well as LOU] which reveals that the Namaqualand cluster is elongated in the N-S direction.

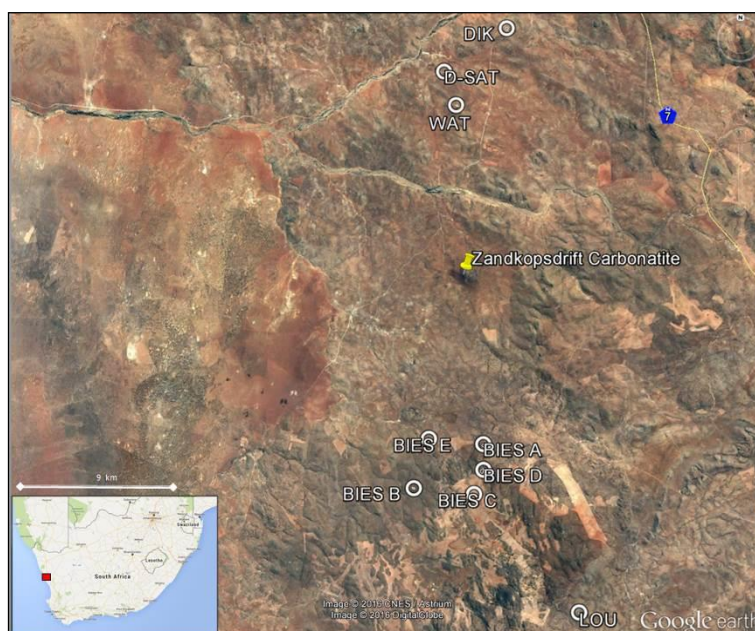


**Figure 11. A Google Earth satellite image showing the location of pipes sampled during this study. The location of the pipes shows that there are three northerly pipes and six pipes in the south of the cluster while the Zandkopsdrift Carbonatite complex occurs within the central region of the cluster.**

Brief field descriptions are provided below, which provide brief descriptions of each sample locality and main observations made for each pipe. A summary of the main differences between the pipes are summarized in Table 1. In this table, abbreviated names are provided for each rock type with the original farm name and these abbreviations are used in this thesis to name the samples.

The petrographic descriptions of the samples collected during this study are provided in Appendix C and other details are provided in Appendix A, which includes the name of each sample, the data collected, the location name and a sample location determined by GPS.

**Table 1. Characteristics of the pipes sampled in the Namaqualand cluster from North to South.**

| Pipes | Farm Name          | Approx. Length (m) | Approx. Width (m) | Type                | Country Rock                                         | Formation           | Group                    | Age              |
|-------|--------------------|--------------------|-------------------|---------------------|------------------------------------------------------|---------------------|--------------------------|------------------|
| DIK   | Dikdoorn           | 150                | 100               | Topographic high    | Basic granulite and amphibolite                      | Mesklip Gneiss      | Little Namaqualand Suite | Mesoproterozoic  |
| DSAT  | Dikdoorn Satellite | 75                 | 40                | Topographic high    | Granitic Gneiss                                      | Mesklip Gneiss      | Little Namaqualand Suite | Mesoproterozoic  |
| WAT   | Watervaal          | 150                | 100               | Topographic high    | Grey equigranular biotite and quartz-feldspar gneiss | Hunboom Gneiss      | Little Namaqualand Suite | Mesoproterozoic  |
| ZAND  | Zandkopsdrift      | ?                  | ?                 | Topographic high    | Granitic Gneiss                                      | Mesklip Gneiss      | Little Namaqualand Suite | Mesoproterozoic  |
| BIESE | Biesiesfontein     | 200                | 150               | Low feature         | Leucocratic, megacrystic granite to gneissic granite | Jakkalshoek Granite | Spektakel Suite          | Mesoproterozoic  |
| BIESA | Biesiesfontein     | 175                | 120               | Topographic high    | Alkali feldspar leucogranite                         | Rietpoort Granite   | Koegel Fontein Complex   | Early Cretaceous |
| BIESD | Biesiesfontein     | 250                | 150               | Topographic high    | Alkali feldspar leucogranite                         | Rietpoort Granite   | Koegel Fontein Complex   | Early Cretaceous |
| BIESB | Biesiesfontein     | 150                | 100               | Low feature         | Leucocratic, megacrystic granite to gneissic granite | Jakkalshoek Granite | Spektakel Suite          | Mesoproterozoic  |
| BIESC | Biesiesfontein     | 50                 | 50                | Low feature         | Alkali feldspar leucogranite                         | Rietpoort Granite   | Koegel Fontein Complex   | Early Cretaceous |
| LOU   | Louisfontein       | 100                | 75                | Depression in slope | Granitic Gneiss                                      | Mesklip Gneiss      | Little Namaqualand Suite | Mesoproterozoic  |

### 3.3.1 DIKDOORN Pipe:

Nine samples were collected from this pipe for this study (DIK-10, DIK-11, DIK-12, DIK-13, DIK-VM1, DIK-VM2, DIK-VM3, DIK-VM4 and DIK-CR1). Google Earth photographs of this pipe are shown below (Figure 12). The top of the photo is facing north. The olivine melilitite-bearing pipe in this locality forms a prominent hill with poor exposure along the contact with the country rock (DIK- CR1). Various types of vesicular melilitite are present within the pipe (DIK-VM1, DIK-VM2, DIK-VM3 and DIK-VM4). The north to north-west side of the pipe has been quarried, which was presumably to use for road aggregate and this has resulted in fairly good exposure of parts of the centre of the pipe which is predominantly massive olivine melilitite. The rock has white fracture-filling calcrete and light brown soil with white calcrete inclusions forming an overlying horizon.

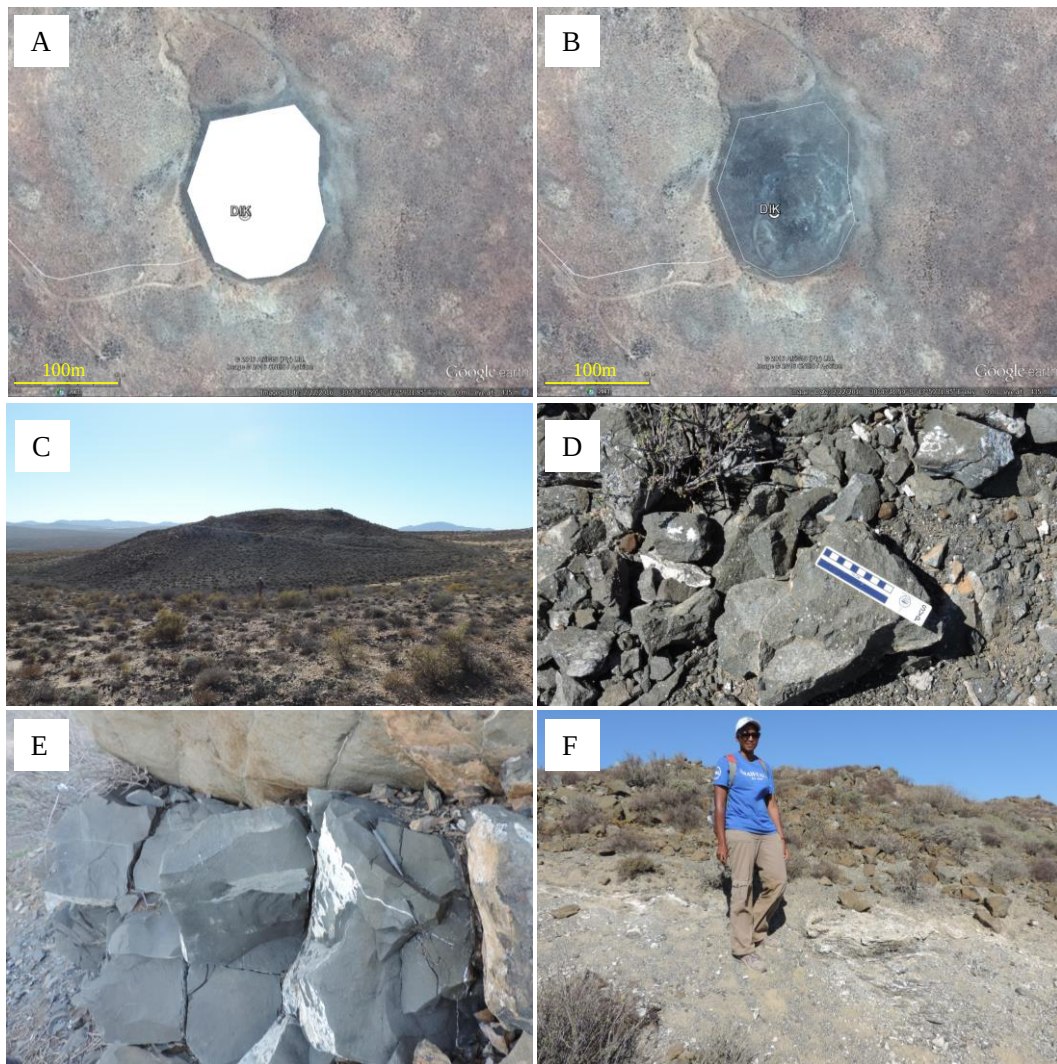


**Figure 12. Dikdoorn pipe showing A). Estimated shape and area of the pipe from a satellite image. B). Satellite image of the pipe shows its outline. C). View towards the east showing the raised topography of the pipe. D). Image showing the fragmented rock found well exposed in the quarry. E). An exposed surface of fresh melilitite within the Dikdoorn pipe quarry.**

### 3.3.2 *DIKDOORN Satellite Pipe:*

Six samples were collected from this pipe for this study (DSAT-1, DSAT-2, DSAT-3A, DSAT-3B, DSAT-4, and DSAT-CR1). Google Earth photographs for this pipe are shown below (Figure 13) in all cases the top of the photo is facing north. The locality appears as a slightly elongated pipe with a ~75 m diameter in the N-S direction. It forms a low hill with exposures of outcropping olivine melilitite in the centre where a trench has been dug and on the southeast part of the pipe where the outcrop is preserved. The rock appears mostly massive in the field, however, the contact was observed between slightly darker (DSAT-3B) and lighter olivine melilitites (DSAT-3A). No contact was observed with the nearby country rock (DSAT-CR1) as the contact is covered by soil and small boulders of olivine melilitite.

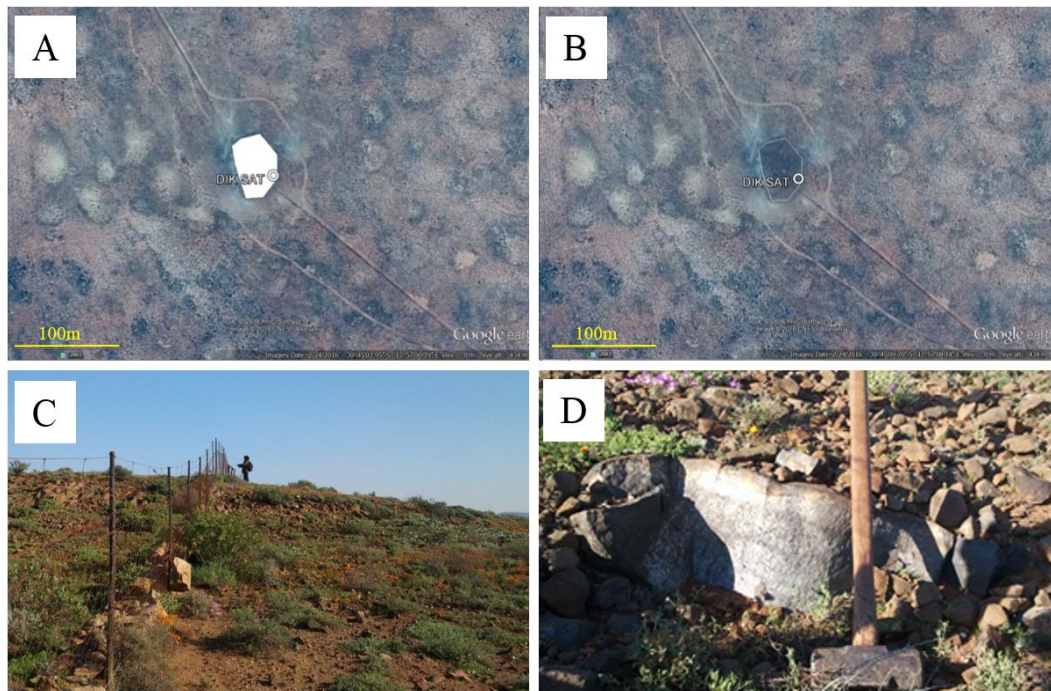


**Figure 13. Dikdoorn Satellite pipe showing: A). the estimated shape and area occupied by the pipe in a satellite image. B). Satellite image of the pipe location. C). Surface of the pipe with small boulders as well isolated outcropping material. D). An in-situ exposure of olivine melilitite.**

### 3.3.3 *Waterval Pipe (WAT):*

Four samples were collected from this pipe during this study (WAT-1, WAT-2, WAT-CR1, and WAT-CR2). Google Earth photographs of this pipe are shown (Figure 14). In all cases, the top of the photo is facing north. The pipe has a 150m long axis and a 100 m width which forms an oval-shaped body trending to the northwest. No photos of samples in the field were taken from this pipe.

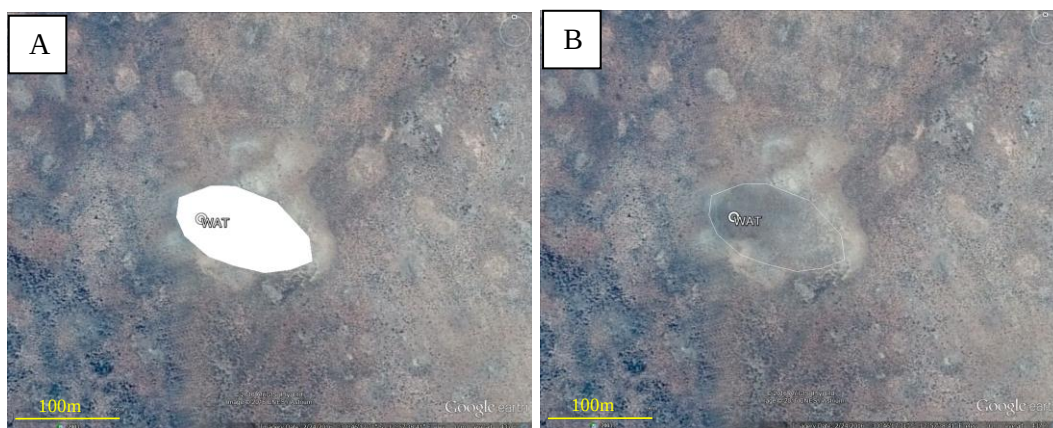


**Figure 14. Waterval pipe showing: A). Estimated shape and area of the pipe in satellite image B). The location of the pipe is shown in the satellite image.**

### 3.3.4 *Zandkopsdrift melilitite pipes (ZAND):*

In addition to the main Carbonatite complex at Zandkopsdrift an occurrence of olivine melilitite was found in an exploration trench and a fresh sample of this was collected and submitted for analysis as part of this study. No field photos were taken and its outline in satellite photos is not clear.

### 3.3.5 *Biesiesfontein pipe E (BIESE):*

Three samples were collected from this pipe for this study (BIESE-1, BIESE-2 and BIESE-3). Google earth photographs of this pipe are shown above (Figure 15). This is one of the larger pipes that were sampled which is ~200 m in diameter in the N-S direction. This pipe forms a flat area with a red-coloured soil horizon that in areas has boulders of olivine melilitite exposed. The contacts between the country rocks are not preserved and no outcrop was found. Visibly fresh material was found in the cores of some of the boulders.

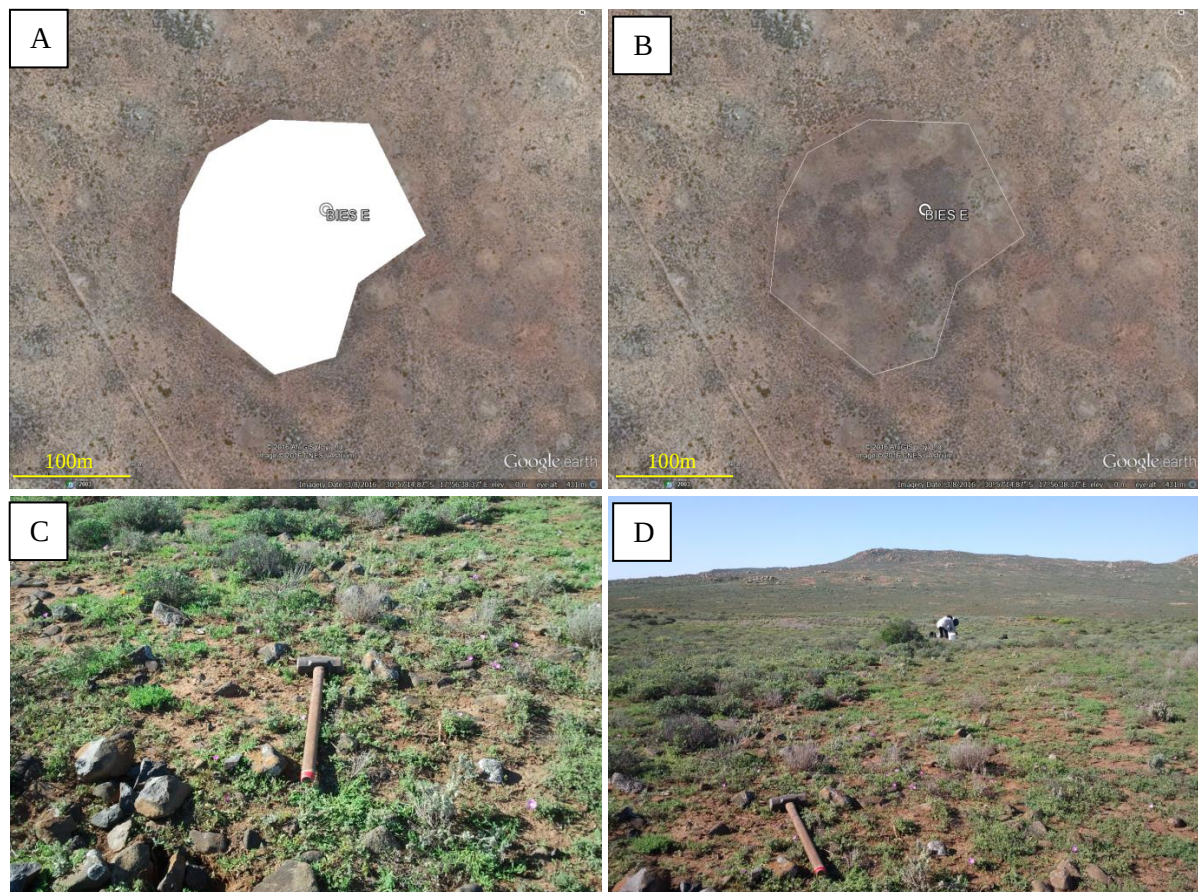


**Figure 15. BIESE pipe showing: A). Estimated area and shape of the pipe in the satellite image. B). The estimated location of the pipe in the satellite image. C). The surface of the pipe shows isolated 20-5 cm melilitite boulders D). Flat surface topography of the pipe with a few isolated boulders and darker red soil.**

### 3.3.6 *Biesiesfontein pipe A (BIESA):*

Five samples were collected from this pipe for this study (BIESA-1, BIESA-2, BIESA-VM1, and BIESA-CR1). Google earth photographs of this pipe are shown below (Figure 16). This pipe occurs as a prominent hill in the landscape with a length of ~175m which is oriented towards the NW. The pipe has a distinct outcrop of olivine melilitite and has areas where vesicular melilitite was found (BIESA-VM1). A country rock sample was collected from the surrounding granites, however, the pipe's contacts with the country rock are obscured by soil that overlies the boundaries of the pipe.

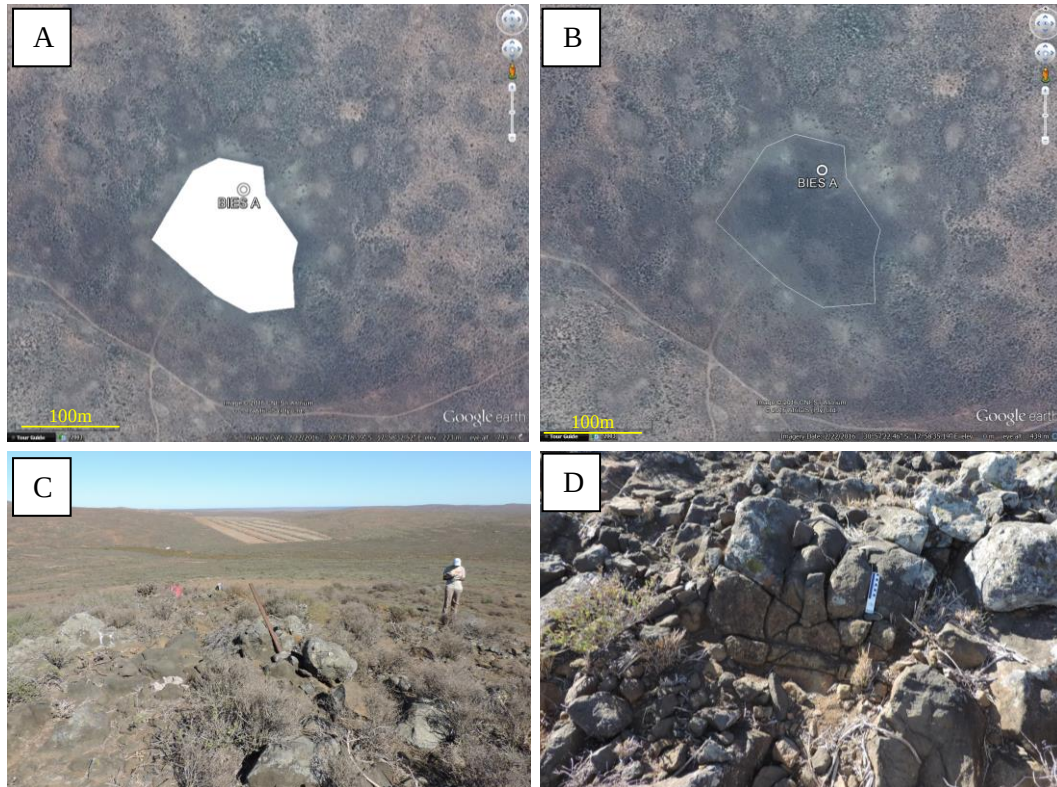


**Figure 16. BIESA pipe showing: A). Pipe shape and area in a satellite image B). Location of the pipe is shown in the satellite image. C). This pipe forms a low rocky hill or rubble-strewn mound of raised topography D). Exposure of the olivine melilitite in places is good with some preserved magmatic banding, otherwise, there are many boulders at surface with fresh interiors.**

### 3.3.7 *Biesiesfontein pipe D (BIESD):*

Six samples were collected from this pipe for this study (BIESD-1, BIESD-2, BIESD-3, BIESD-4, BIESD-CR1, and BIESD-CR2). Google earth photographs of this pipe are shown below (Figure 17). This pipe has a length of ~250 m and a width of 150 m and is relatively flat with no exposure and poorly defined contacts. The surface of the pipe is covered with red soil and boulders of olivine melilitite of <20 cm. Some areas of the pipe have white fragments of calcite suggesting the development of a calcite horizon above the pipe.

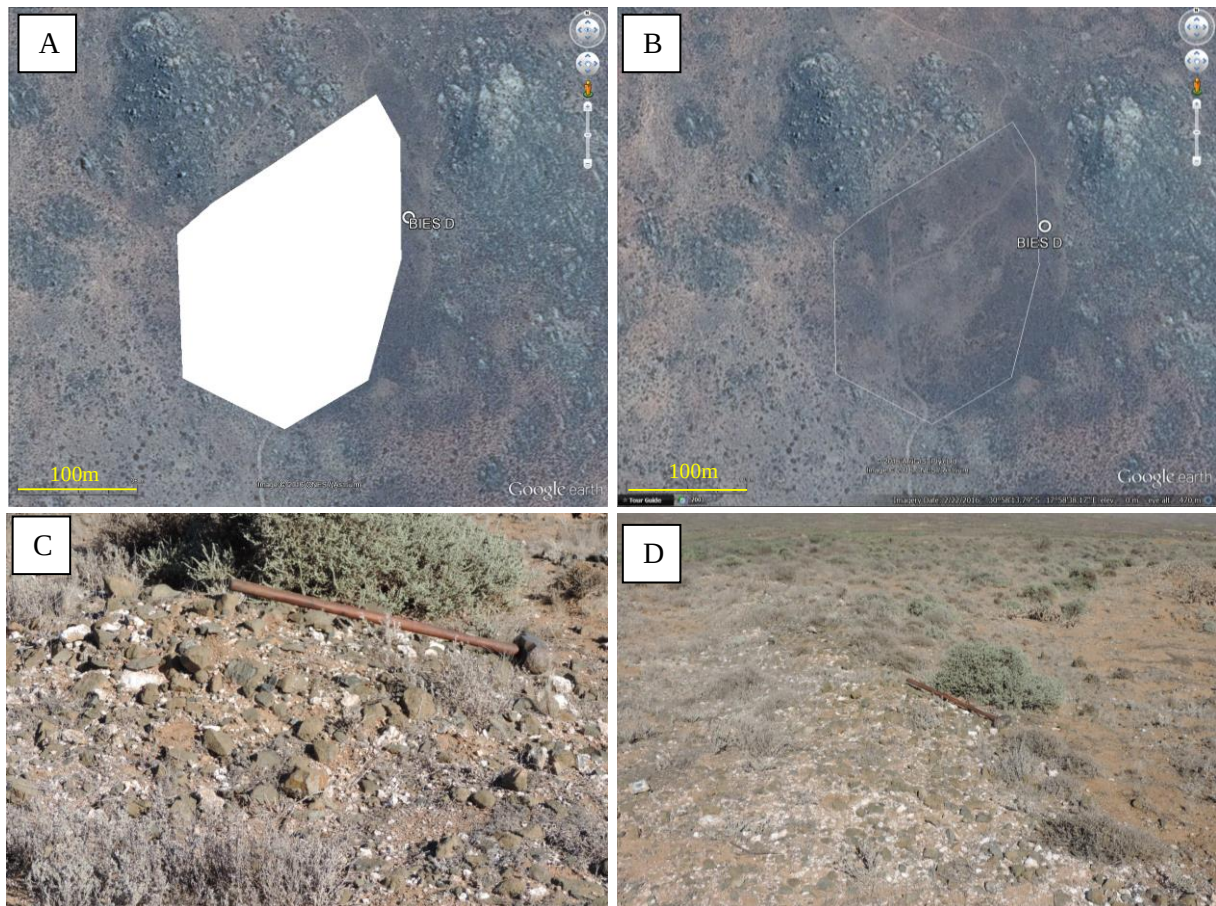


**Figure 17. BIESD pipe showing: A). The approximate shape and surface area of the pipe are shown in the satellite image. B). The location of the pipe is shown in a satellite image. C). A low mound of melilitite showing the presence of calcrete with the boulders D). The surface topography of the pipe shows a low flat surface with some calcrete developed around the boulders.**

### 3.3.8 *Biesiesfontein pipe B (BIESB):*

Three samples were collected from this pipe for this study (BIESB-1, BIESB-2 and BIESB-3). Google earth photographs of this pipe are shown below (Figure 18). This pipe has an elongated shape and is oriented towards the NW with a ~150 m diameter length and a 100 m diameter width. The pipe is mostly preserved as flat low-lying soil-covered material, however, some of the melilitite is exposed in the road as a distinct outcrop. The rock appears massive in outcrop and has well-developed joints.

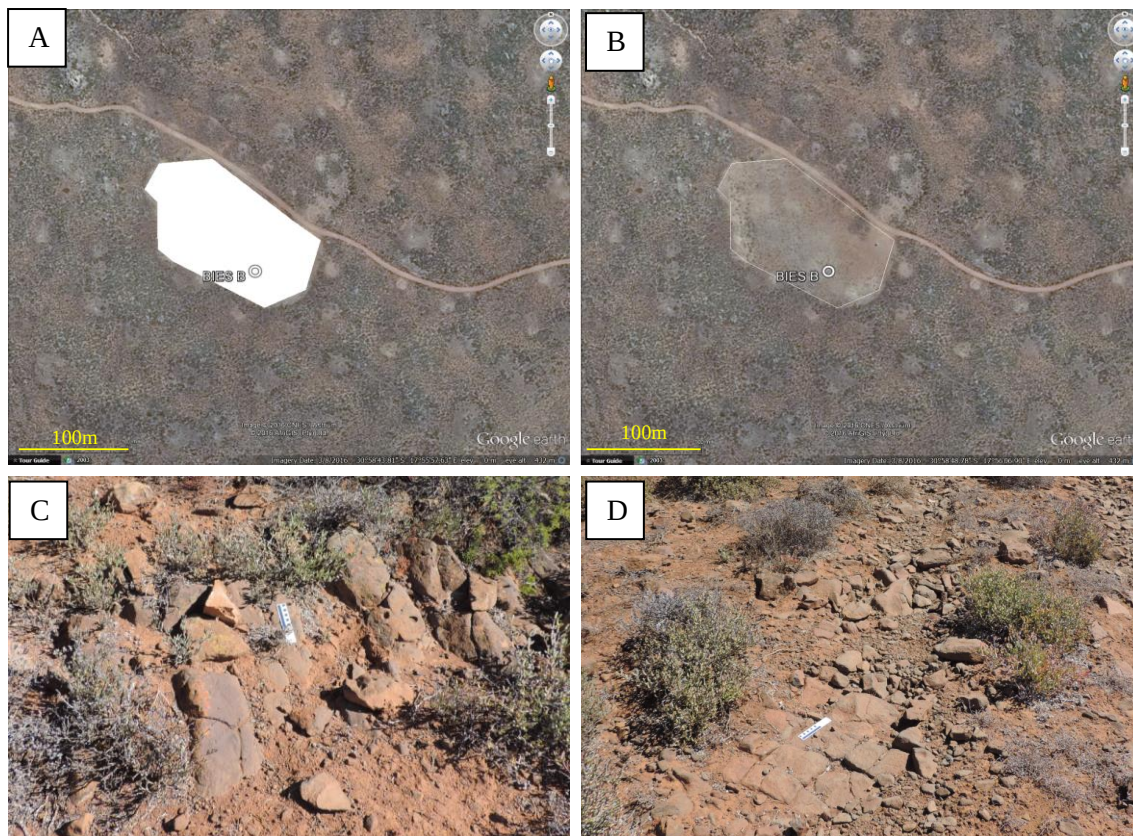


**Figure 18. BIESB pipe showing: A). The estimated shape and surface area of the pipe in the satellite image. B). The approximate location of the pipe in the satellite image. C). Some exposure of the pipes at surface shows weathering pits from the erosion of certain minerals. D). The surface of the pipe has a flat topography with some outcrop and a slight slope to the surrounding landscape.**

### 3.3.9 *Biesiesfontein pipe C (BIESC):*

Three samples were collected from this pipe for this study (BIESC-1, BIESC-2 and BIESC-3). Google earth photographs of this pipe are shown below (Figure 19). This pipe is the least well-exposed and most poorly preserved pipe that was observed in the Namaqualand region during this

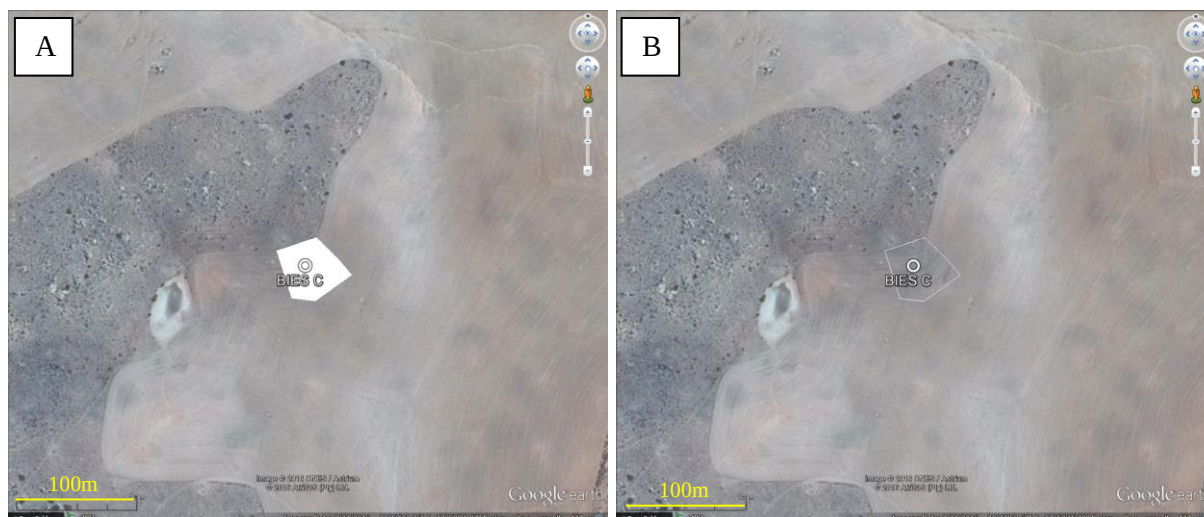


**Figure 19. BIESC pipe showing: A). Estimated shape and area of the pipe. B). Approximate location of the pipe. The pipe locality was disturbed by agricultural activity but at surface boulders of olivine melilitite were found which were assumed to correlate to the location of the pipe.**

study. All that remains of the pipe are fragments and boulders of the olivine melilitite within a red soil found in an area of ploughed soil. While the exact size of the pipe is uncertain, it was estimated to be ~50m by 50m.

### 3.3.10 *Louisfontein Pipe (LOU):*

Five samples were collected from this pipe for this study (LOU-1, LOU-2, LOU-3, LOU-4, and LOU-CR-1). Google earth photographs for this pipe are shown below (Figure 20) in all cases the top of the photo is facing north. The photos show that the pipe had no distinct outcrop and occurred on the northeast side of a hill with a quartz vein and a dyke of altered mafic rock (LOU-1) at the top. Most of the pipe is covered by red soil and scattered vegetation with only a few outwardly weathered boulders of a maximum of 30 cm diameter at the surface. The boulders were sampled as they appeared to be fresh in their core regions.

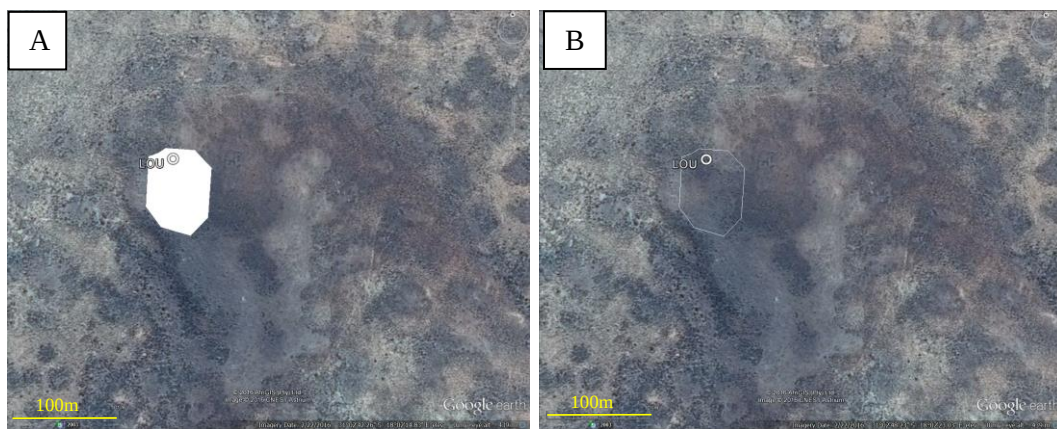


**Figure 20. LOU Pipe showing: A). Estimated pipe shape and area on the satellite map. B) Estimated pipe location on a satellite map. The Surface topography of the pipe shows a slope towards the south-east.**

## 3.4. Sample preparation:

The samples were photographed before or after being split using a hydraulic splitter. An attempt was made to process only a portion of each sample, usually half of each specimen or half of the freshest material, in order to preserve material for possible future research. The fragments that were identified to be weathered (e.g., outer portions and containing veins) were not used further. A ~1 cm by ~0.75 cm thick slab was cut for thin section petrography.

After splitting into roughly cubic or irregular shapes small enough to fit into the jaw crusher, (typically no more than 1-2 cm in maximum dimension), the split material was visually inspected and visibly altered material was set aside. The remainder was then crushed in a carbon steel laboratory jaw crusher to create rock chips with a maximum dimension of  $\approx 1$  cm. A roughly 500g portion was hand-picked so as to exclude weathered or altered pieces, and those containing veins, xenoliths and vesicle fillings. For most samples, all of the chips included in the milled fraction had a dark grey, “sugary” appearance indicative of fresh mineral phases, with no xenoliths, veins or vesicles. However, in the

case of the vesicular melilitites, even the freshest material was moderately altered and often contained small amounts of vesicle fillings.

The freshest available sample fraction was then further split and a ~100 g portion was finely milled (to < 25  $\mu\text{m}$ ) in a carbon steel disk mill. The milled material was used for geochemical analysis, while the remaining fresh material was crushed for use in mineral separation.

### **3.5. Optical Petrography:**

Petrographic analysis was performed on thin sections created from fresh portions of each rock. The thin sections were examined under transmitted and reflected light microscopy to examine the mineralogy and texture of transparent/translucent (mainly silicate) minerals and mainly opaque oxide minerals, respectively. Petrography was used to provide an indication of the mineral compositions in samples as well as the variation between them in terms of modal mineralogy and texture.

### **3.6. Mineral analysis by electron microprobe:**

The compositions of the main mineral phases present in melilitite samples were determined using a JEOL JXA 8100 electron probe micro-analyser instrument in the Department of Geological Sciences, UCT. For this study, thin sections from four samples (each from a different pipe) were selected for analysis to provide an indication of the chemical composition of the main phenocryst minerals present in these four pipes. It should be noted that the work of Moore (1979) and several subsequent papers (Moore and Erlank, 1979; etc.) dealt extensively with mineral chemistry of Namaqualand melilitites (particularly for olivine), and the mineral chemistry data obtained in this thesis are primarily intended to complement this older data set by including data for melilitite pipes that were not investigated in the earlier study (e.g., LOU and DSAT) or samples that are more or less differentiated than the Namaqualand melilitite samples investigated by Moore and others.

The minerals for which data are provided are olivine, Fe-Ti oxides, phlogopite, clinopyroxene and melilite. The results are compared with previous mineral chemistry data presented by Moore (1979), Moore (1981), Moore (1983) and Boctor and Yoder (1983) for several pipes in the Namaqualand and Bushmanland clusters. All analyses were performed with a beam current of 20 nA and an accelerating voltage of 15 kV. Table 2 gives the standards used for the calibration of each oxide measured for each mineral routine.

**Table 2: Mineral standards used for electron microprobe calibration.**

| Mineral:                       | Olivine | Melilite | Mica | Fe-oxide |
|--------------------------------|---------|----------|------|----------|
| SiO <sub>2</sub>               | M-OL    | JJGCPX   | K-H  | K-P      |
| TiO <sub>2</sub>               | RUT     | RUT      | RUT  | RUT      |
| Al <sub>2</sub> O <sub>3</sub> | K-P     | CHRO     | K-H  | CHRO     |
| Cr <sub>2</sub> O <sub>3</sub> | CHRO    | n.a.     | n.a. | CHRO     |
| FeO                            | M-OL    | K-P      | K-H  | ILMT     |
| MnO                            | RHOD    | RHOD     | RHOD | RHOD     |
| MgO                            | M-OL    | JJGCPX   | K-H  | CHRO     |
| CaO                            | K-P     | JJGCPX   | K-H  | K-P      |
| NiO                            | NISI    | n.a.     | n.a. | n.a.     |
| Na <sub>2</sub> O              | n.a.    | K-H      | K-H  | n.a.     |
| K <sub>2</sub> O               | n.a.    | AMPH     | K-H  | n.a.     |
| F                              | n.a.    | n.a.     | FLUR | n.a.     |

**Abbreviations\*:**

|               |                                          |
|---------------|------------------------------------------|
| <b>M-OL</b>   | <b>Marjalahti olivine (Smithsonian)</b>  |
| <b>RUT</b>    | <b>Rutile (Smithsonian)</b>              |
| <b>CHRO</b>   | <b>42NL11 chromite (Carnegie)</b>        |
| <b>RHOD</b>   | <b>Rhodochrosite (in-house standard)</b> |
| <b>K-P</b>    | <b>Kakanui pyrope (Smithsonian)</b>      |
| <b>K-H</b>    | <b>Kakanui hornblende (Smithsonian)</b>  |
| <b>AMPH</b>   | <b>Amphibole (in-house standard)</b>     |
| <b>NISI</b>   | <b>High nickel silicate</b>              |
| <b>FLUR</b>   | <b>Fluorite (in-house standard)</b>      |
| <b>ILMT</b>   | <b>Ilmenite (in-house standard)</b>      |
| <b>JJGCPX</b> | <b>JJG1424 clinopyroxene (in-house)</b>  |
| <b>n.a.</b>   | <b>not analysed</b>                      |

*\*Mineral standards were analysed as unknowns to check precision and accuracy. Olivine (M-OL) was used for this purpose for olivine, whereas haematite was used for Fe-oxides and plagioclase was used for melilite, as there was no melilite standard. Appendix G shows the average values obtained for the standards during the electron microprobe analysis.*

### 3.7. Whole-rock Geochemical Analysis:

The whole rock geochemical analysis includes the major element, trace element and radiogenic isotope compositions (Pb, Sr and Nd) of the rock samples. This data was used to geochemically characterize and compare these rocks with previous findings. The whole rock analysis was performed on powders prepared from splits of carefully picked fresh material.

#### 3.7.1 Major and trace element Analysis by XRF:

Major element oxide concentrations were obtained by XRF methods conducted on ~2 g of whole rock powder sample. Fusion disks were used to measure the major element oxide concentrations, in which a Li-tetraborate-Li-metaborate flux (in the ratios 57:43 respectively) and a LiBr releasing agent were used. The powdered samples were weighed out and then dried overnight at 110°C to obtain wt.% of adsorbed volatiles (wt.% H<sub>2</sub>O-) then roasted at 800°C for four hours to record “loss on ignition” (e.g., weight loss due to volatilized H<sub>2</sub>O, carbonate, organics and sulphur). Samples were weighed

before and after each heating/roasting operation to gauge the weight lost. The roasted powder was used to make the fused disks by diluting 0.7 g with 6 g of the flux, which was then melted in a platinum crucible in an automated Claise M4 Fluxer. The molten samples were then poured out into a mould to make a glass disk.

A Panalytical Axios wavelength-dispersive XRF spectrometer was then used to measure the major element concentrations from the fusion disks using standard techniques and a calibration curve, assembled using a series of rock standard powders prepared similarly to the samples, was used to convert corrected intensities to weight percent values.

### **3.7.2 *Trace Element Analysis by Pressed Pellet XRF:***

Trace element analysis was conducted for Sc, Cr, V, Mn, Co, Ni, Mo, Cu, Zn, Rb, Sr, Y, Zr, Nb, Ba, Pb, Th, U, Cl and F by XRF on ~6 g of powder from each sample made into pressed pellets. These pellets were prepared using a drop of polyvinyl alcohol as a binder added to the powder and pressed in a die in a laboratory press under 10 tons of pressure to make the pellets. The XRF measurements were performed using the same Panalytical Axios XRF spectrometer used for the major elements. For all elements, corrected intensities were obtained by correcting raw intensities for background, composition-dependent mass absorption and enhancement effects (with these corrections determined either from the Rh-K  $\beta$  Compton peak or calculated from the major element composition) and corrected for spectral overlap effects, such as Rb-K  $\beta$  on Y-K $\alpha$ . Similarly, to the major element measurements, corrected trace element intensities were converted to elemental concentrations using calibration curves based on the analysis of international rock standards.

### **3.7.3 *Trace Element Analysis by ICP-MS:***

Analysis by inductively coupled plasma-mass spectrometry (ICP-MS) of low abundance trace elements including the rare earth elements (REE), Cs, Hf, Ta, Pb, Th and U, as well as several of the high-abundance trace elements also analysed by XRF (e.g., Rb, Sr, Nb, Zr, Y) was performed using a Thermo X-Series 2 quadrupole ICP-MS instrument at the UCT Department of Geological Sciences. Aliquots of 0.05 g of sample powder were digested under high pressure and temperature conditions. This was done using a 4:1 mixture of hydrofluoric and nitric acids in loosely sealed 3 ml PFA Teflon beakers placed inside clean PTFE Teflon capsules inside 30 ml Parr steel digestion vessels. After loading, the digestion vessels were tightened and placed in an oven at 200°C for 18-24 hours. After digestion, the resulting solutions were dried down on a hot plate at 100°C and re-suspended twice in ultra-pure concentrated nitric acid to remove fluorides. After drying down the solutions a final time, they were diluted 10 000-fold with a 5% dilute nitric acid solution spiked with 10ppm of the internal standard elements Rh, In, Re and Bi for analysis by quadrupole ICPMS.

Analysis of the sample solutions was performed in peak-jumping mode on the Thermo X-Series 2 quadrupole ICP-MS. For each sample, the analysis consisted of 3 sets of 100 sweeps across the mass

spectrum, with dwell times of 40 milliseconds on each selected atomic mass (including analyte isotopes, internal standards and interferences). The resulting ion intensities were converted into concentrations using a blank solution and six synthetic calibration standards, of increasing concentration, prepared from certified multielement standard solutions.

**Table 3: Results for the replicate analysis of standards used during the ICP-MS analysis.**

| Element: | V5 measured: | %RSD (1s): | *V5 accepted: | Element: | BHVO-1 measured: | %RSD (1s): | BHVO-1 accepted: | Element: | AGV-1 measured: | %RSD (1s): | AGV-1 accepted: |
|----------|--------------|------------|---------------|----------|------------------|------------|------------------|----------|-----------------|------------|-----------------|
| Sc       | 38.3         | 7.3        | 37.6          | Sc       | 32.4             | 6.1        | 31.8             | Sc       | 11.7            | 5.0        | 12.6            |
| V        | 253          | 4.9        | 250           | V        | 318              | 2.1        | 321              | V        | 123             | 2.1        | 126             |
| Cr       | 247          | 1.6        | 249           | Cr       | 277              | 1.3        | 289              | Cr       | 8.64            | 4.8        | 9.0             |
| Co       | 35.8         | 1.1        | 44            | Co       | 37.1             | 4.6        | 45               | Co       | 12.9            | 4.2        | 15.3            |
| Ni       | 94.6         | 5.8        | 98            | Ni       | 118              | 3.2        | 120              | Ni       | 5.22            | 4.4        | 16              |
| Cu       | 56.3         | 3.4        | 46            | Cu       | 152              | 3.4        | 136              | Cu       | 61.6            | 5.6        | 58              |
| Zn       | 104          | 5.6        | 90            | Zn       | 107              | 1.9        | 105              | Zn       | 92.9            | 3.2        | 87              |
| Rb       | 2.98         | 3.4        | 2.98          | Rb       | 9.51             | 4.3        | 9.5              | Rb       | 67.8            | 4.6        | 68.3            |
| Sr       | 206          | 4.1        | 203           | Sr       | 403              | 3.6        | 390              | Sr       | 662             | 3.7        | 655             |
| Y        | 37.6         | 3.5        | 37.9          | Y        | 26.6             | 3.0        | 28               | Y        | 19.3            | 1.9        | 21              |
| Zr       | 172          | 3.8        | 175           | Zr       | 173              | 3.1        | 180              | Zr       | 217             | 2.7        | 240             |
| Nb       | 8.21         | 3.5        | 8.46          | Nb       | 18.9             | 2.7        | 19.5             | Nb       | 13.9            | 2.6        | 14.9            |
| Cs       | 0.038        | 16.8       | 0.035         | Cs       | 0.107            | 19.9       | 0.10             | Cs       | 1.27            | 18.5       | 1.3             |
| Ba       | 30.0         | 2.8        | 29.9          | Ba       | 129              | 1.5        | 133              | Ba       | 1209            | 1.4        | 1223            |
| La       | 8.23         | 2.5        | 8.02          | La       | 15.3             | 1.5        | 15.5             | La       | 38.2            | 1.1        | 38.5            |
| Ce       | 22.7         | 2.1        | 22.5          | Ce       | 37.8             | 1.5        | 38               | Ce       | 68.0            | 1.0        | 68.5            |
| Pr       | 3.43         | 3.4        | 3.42          | Pr       | 5.25             | 1.7        | 5.45             | Pr       | 8.08            | 1.8        | 8.45            |
| Nd       | 16.8         | 3.0        | 16.7          | Nd       | 23.4             | 2.2        | 24.7             | Nd       | 31.5            | 1.2        | 31.6            |
| Sm       | 4.93         | 3.2        | 4.98          | Sm       | 6.08             | 2.8        | 6.17             | Sm       | 5.63            | 2.6        | 5.82            |
| Eu       | 1.80         | 3.0        | 1.75          | Eu       | 1.95             | 3.7        | 2.06             | Eu       | 1.55            | 5.2        | 1.57            |
| Gd       | 6.30         | 3.7        | 6.14          | Gd       | 6.21             | 3.7        | 6.22             | Gd       | 4.68            | 3.0        | 4.73            |
| Tb       | 1.10         | 2.1        | 1.06          | Tb       | 0.912            | 2.3        | 0.95             | Tb       | 0.651           | 3.2        | 0.664           |
| Dy       | 6.92         | 2.5        | 6.81          | Dy       | 5.25             | 2.9        | 5.25             | Dy       | 3.54            | 1.5        | 3.54            |
| Ho       | 1.44         | 2.5        | 1.41          | Ho       | 0.97             | 2.7        | 1                | Ho       | 0.68            | 1.7        | 0.690           |
| Er       | 4.19         | 2.1        | 3.99          | Er       | 2.53             | 2.7        | 2.56             | Er       | 1.84            | 1.8        | 1.86            |
| Tm       | 0.61         | 3.5        | 0.60          | Tm       | 0.331            | 5.0        | 0.33             | Tm       | 0.26            | 2.1        | 0.280           |
| Yb       | 3.80         | 1.0        | 3.71          | Yb       | 1.97             | 1.0        | 1.98             | Yb       | 1.61            | 1.1        | 1.64            |
| Lu       | 0.60         | 2.2        | 0.56          | Lu       | 0.285            | 4.7        | 0.278            | Lu       | 0.25            | 2.7        | 0.248           |
| Hf       | 3.99         | 2.2        | 4.08          | Hf       | 4.16             | 1.2        | 4.3              | Hf       | 4.92            | 1.3        | 5.0             |
| Ta       | 0.50         | 3.5        | 0.50          | Ta       | 1.23             | 10.7       | 1.2              | Ta       | 0.893           | 11.0       | 0.882           |
| Pb       | 0.93         | 4.2        | 0.92          | Pb       | 1.94             | 3.1        | 2.1              | Pb       | 35.8            | 0.1        | 37.3            |
| Th       | 0.48         | 2.7        | 0.47          | Th       | 1.22             | 2.3        | 1.26             | Th       | 6.37            | 1.4        | 6.53            |
| U        | 0.18         | 1.3        | 0.19          | U        | 0.432            | 9.5        | 0.42             | U        | 1.85            | 3.8        | 1.89            |

*\*Table summarizes data for 5-7 analyses of each rock standard, measured at the same time as the samples.*

*\*Accepted values are from Janney et al. (2005), as well as Le Roux et al. (2002) for some elements not present in the Janney et al. (2005) compilation.*

*\*Accepted values for BHVO-1 and AGV-1 are preferred values from the GeoREM website (<http://georem.mpch-mainz.gwdg.de>)*

These standard solutions spanned a concentration range of nearly three orders of magnitude and all analyte intensities in all samples fell within the calibrated range. The quality of the results was monitored by analysing the USGS rock standards BHVO-1 (Hawaiian basalt) and AGV-1 (Guano Valley andesite, GeoREM preferred values used for both, <http://georem.mpch-mainz.gwdg.de>) and the UC in-house mid-ocean ridge basalt glass standard V5-40-56 (e.g., Janney et al., 2005). The analytical

uncertainties based on replicate analyses of these standards were found to be within about 5% relative (2s) for the rare earth elements and Ba and somewhat higher for other elements, particularly U, Ta, Cs and some transition metals (Table 3). Detection limits were in the sub-ppb range for concentrations in the rock samples.

### 3.7.4 ***Radiogenic Isotope measurement by MC-ICP-MS:***

#### **Elemental separation**

The radiogenic isotopes were measured on the residues of the high-pressure acid-digested samples used to conduct the trace element analysis by ICPMS. After drying, the residual samples were converted from nitrate to chloride and then to bromide form (by suspension in hydrochloric and hydrobromic acids, respectively) for Pb separation chemistry. Pb was separated from the other elements using AG1x8 anion exchange resin. The residue from Pb chemistry was then converted back to chloride using concentrated hydrochloric acid, dried down, diluted in 1 M HCl-0.1M HF and passed through primary columns using AG50x8 cation exchange resin to collect Hf (not analysed in this study), Sr and the rare earth elements collecting these elements in 2.5 M and 4 M HCl, respectively. Finally, the REE fraction was dried down and Nd was separated using columns filled with EiChrom™ Ln-spec resin in a medium of 0.25M HCl.

#### **Mass spectrometry**

Sr, Nd and Pb isotope ratios were all determined by solution multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) employing a NuPlasma HR MC-ICP-MS instrument. Isotope ratios of each element were measured in separate sessions and the measured ratio was normalised to published values for isotopic standards (NBS 987 for Sr, J-Ndi for Nd and NBS 981 for Pb). Standard isotope ratios values are:

- $^{87}\text{Sr}/^{86}\text{Sr}$  for NBS987 is 0.710255 (Tanaka *et al.*, 2000).
- $^{143}\text{Nd}/^{144}\text{Nd}$  for JNdi-1 is 0.512115 (Tanaka *et al.*, 2000).
- $^{206}\text{Pb}/^{204}\text{Pb}$  for NBS981 is 16.9405 (Galer and Abouchami, 1998).
- $^{207}\text{Pb}/^{204}\text{Pb}$  for NBS981 is 15.4963 (Galer and Abouchami, 1998).
- $^{208}\text{Pb}/^{204}\text{Pb}$  NBS981 is 36.7219 (Galer and Abouchami, 1998).

For Sr and Nd, instrumental mass fractionation (mass bias) was corrected by internal normalization using the ratios of two stable, non-radiogenic isotopes for each element:  $^{86}\text{Sr}/^{88}\text{Sr}$  ( $=0.1194$ ) for Sr and  $^{146}\text{Nd}/^{144}\text{Nd}$  ( $=0.7325$ ) for Nd. As Pb only has one stable non-radiogenic isotope, mass bias correction was applied externally by adding NBS 997 Tl and using the accepted  $^{203}\text{Tl}/^{205}\text{Tl}$  ratio for this element, with the implicit assumption that the mass bias correction for Tl was the same as that for Pb.

### 3.8. Oxygen Isotope Analysis of Olivine Grains:

#### 3.8.1 Olivine separation:

Samples used for oxygen isotope analysis were selected based on the basis of (1) their geographical location, to get a selection of samples from across the Namaqualand melilitite cluster, and (2) their whole-rock composition, to select samples with a range in Mg #'s (as a proxy for extent of magma evolution) and (3) their modal mineralogy, to select samples with relatively fresh olivine grains. A representative ~200 g split of fresh rock chips (+1 cm) from these samples was crushed in a steel jaw crusher such that ~70 percent of the material passed through a 2 mm screen. The -2 mm material was screened again at 600  $\mu\text{m}$  to create three size fractions (+2 mm, -2mm/+600  $\mu\text{m}$ , -600 $\mu\text{m}$ ). The -600  $\mu\text{m}$  size fractions were washed with water to remove fine dust particles and then dried.

Some of the resulting size fractions were examined for liberated (free) olivine grains which could be used for oxygen isotope analysis. The focus was placed on the coarse-size fractions to collect the largest olivine grains. In most samples, the olivine grains in the -600  $\mu\text{m}$  fraction were not picked out as sufficient grains were found in +600  $\mu\text{m}$  fraction to conduct the initial oxygen isotope analysis. Liberated olivine grains were picked out from the material and washed in ethanol to remove surface contaminants such as oils or fine dust particles picked up during crushing and separation.

### 3.9. Oxygen Isotope Analysis by Laser Fluorination:

Olivine separates (typically 2-3 mg) extracted from the olivine melilitite samples were analysed for oxygen isotopes using laser fluorination methods which have been described by Harris and Vogeli (2010). After separation, the olivine separates were cleaned with ethanol and placed in a polished nickel sample holder with multiple wells (one per sample) along with (2-3 mg) of the in-house standard (Monastery Garnet, MON GT). To remove any moisture from the sample, the sample holder and the grains contained within it were dried in a 110°C oven for >2 h before being placed into the reaction chamber. During the reaction with 10 kPa of  $\text{BrF}_5$ , the  $\text{O}_2$  formed from each sample was purified by passing through a KCl trap and collected onto 5Å molecular sieve in a glass storage bottle.

Measurements of oxygen isotopes in the glass bottles were done using a gas-source mass spectrometer in dual inlet mode in the Archaeology department at U.C.T. The oxygen isotope variations for a sample are described as a ratio of  $^{18}\text{O}$  to  $^{16}\text{O}$  that is reported in delta notation which is traditionally used in isotope geochemistry.

$$\delta^{18}\text{O} = (\text{R}_{\text{SA}}/\text{R}_{\text{ST}} - 1) \times 1000$$

where  $\text{R}_{\text{SA}}$  and  $\text{R}_{\text{ST}}$  are absolute ratios of  $^{18}\text{O}/^{16}\text{O}$  in sample ( $\text{R}_{\text{SA}}$ ) and standard ( $\text{R}_{\text{ST}}$ ). The standard used is SMOW which stands for Standard Mean Ocean Water (Bindeman, 2008). The raw  $\delta^{18}\text{O}$  value of average MON GT, whose value relative to SMOW is well-characterised, was used to calculate the  $\delta^{18}\text{O}$  value of each sample relative to SMOW.

MON GT was calibrated on the UCT laser system against UWG-2 garnet standard ( $\delta^{18}\text{O} = 5.80\text{‰}$ ) from Valley *et al.* (1995). An average  $\delta^{18}\text{O}$  value of  $5.38\text{‰}$  obtained for MON GT was used to normalise the raw data to the SMOW scale (Harris and Vogeli, 2010). The long-term  $2\sigma$  uncertainty in  $\delta^{18}\text{O}$  MON GT standards run with each batch of 10 samples is  $0.11\text{‰}$  ( $n = 216$ ), corresponding to a  $2\sigma$  value of  $0.16\text{‰}$  with reference to the same method and instrumentation followed by Harris *et al.* (2015).

## 4. PETROGRAPY AND MINERAL CHEMISTRY:

According to various models and normative mineralogical criteria outlined below, the samples studied from the Namaqualand pipes include olivine melilitites, olivine nephelinites and nephelinites. However, for the sake of simplicity, unless otherwise stated, the term "melilitite" (*sensu lato*) is used to refer to these igneous rock samples as a group. Therefore, these rock types are grouped together and described by locality as the Namaqualand melilitites or Bushmanland melilitites.

### 4.1. Petrographic results for the Namaqualand melilitites.

The petrographic descriptions for the Namaqualand melilitites investigated in this study are summarized in Table 4. The samples are all dark grey to dark brown, fine- to very fine-grained rocks (i.e., with average grain sizes of less than 1mm) with coarser olivine phenocrysts set in a finer-grained aphanitic matrix. Half of the samples are melilite-free or contain less than 10 % melilite and hence are classed as nephelinites or olivine nephelinites, rather than olivine melilitites which must have both  $\geq 10\%$  melilite and  $\geq 10\%$  olivine, based on the criteria of Le Bas and Streckeisen (1991).

Based on these criteria, samples from pipes BIESA and BIESD, are classified as olivine nephelinites, those from BIESE and DSAT are classified as nephelinites, while the samples from the BIESB, BIESC, LOU and WAT pipes are classified as olivine melilitites. Pipe DIK is the only one of the localities studied that contains more than one rock type: olivine nephelinites and olivine melilitites.

**Table 4. Rock types for samples are determined by modal mineralogy (Le Maitre, 2002).**

| Pipe  | Sample Name               | Rock Type           | Matrix            |
|-------|---------------------------|---------------------|-------------------|
| DIK   | DIK-10 A, B               | Olivine Melilitite  | Very Fine-grained |
|       | DIK-11A,11B, 12A, 12B, 13 | Olivine Nephelinite | Very Fine-grained |
|       | DIK-VM1,2,3,4             | Olivine Melilitite  | Fine-grained      |
| DSAT  | DSAT-1,4                  | Nephelinite         | Fine-grained      |
|       | DSAT-2,3A,3B              | Nephelinite         | Fine-grained      |
| WAT   | WAT-1,2                   | Olivine Melilitite  | Very Fine-grained |
| ZAND  | ZAND-7                    | Olivine Melilitite  | Fine-grained      |
| BIESE | BIESE-1,2,3               | Nephelinite         | Fine-grained      |
| BIESA | BIES-10,11                | Olivine Nephelinite | Very Fine-grained |
|       | BIESA-1,2                 | Olivine Nephelinite | Very Fine-grained |
|       | BIESA-VM1                 | Olivine Nephelinite | Fine-grained      |
| BIESD | BIESD-1,2,3,4             | Olivine Nephelinite | Very Fine-grained |
| BIESB | BIESB-1,2,3               | Olivine Melilitite  | Very Fine-grained |
| BIESC | BIESC-1,2,3               | Olivine Melilitite  | Very Fine-grained |
| LOU   | LOU-2,3,4                 | Olivine Melilitite  | Fine-grained      |

*\*fine-grained 1 to 0.5 mm*

*\*\*very fine-grained is less than 0.5 mm*

Most very fine-grained samples (<0.5 mm) are olivine nephelinites whereas simply fine-grained samples (< 1 mm and >0.5) are olivine melilitites (Table 4). The only significant distinction between the olivine nephelinites and olivine melilitites in terms of mineralogy or texture is the presence and/or abundance of melilite. Olivine melilitites and olivine nephelinites have > 10% olivine and similar mineralogy except, olivine melilitites are those with more than 10 vol. % melilitite (Moore, 1979; Le Maitre, 2002) while those with less than 10 % melilite are classified as olivine nephelinites. Based on observations of these samples and from other studies, the olivine nephelinites characteristically have a higher modal amount of clinopyroxene which is typically coarser-grained in the nephelinites than in the olivine melilitites (Moore, 1979). The olivine melilitites typically have finer-grained clinopyroxene or are clinopyroxene-free.

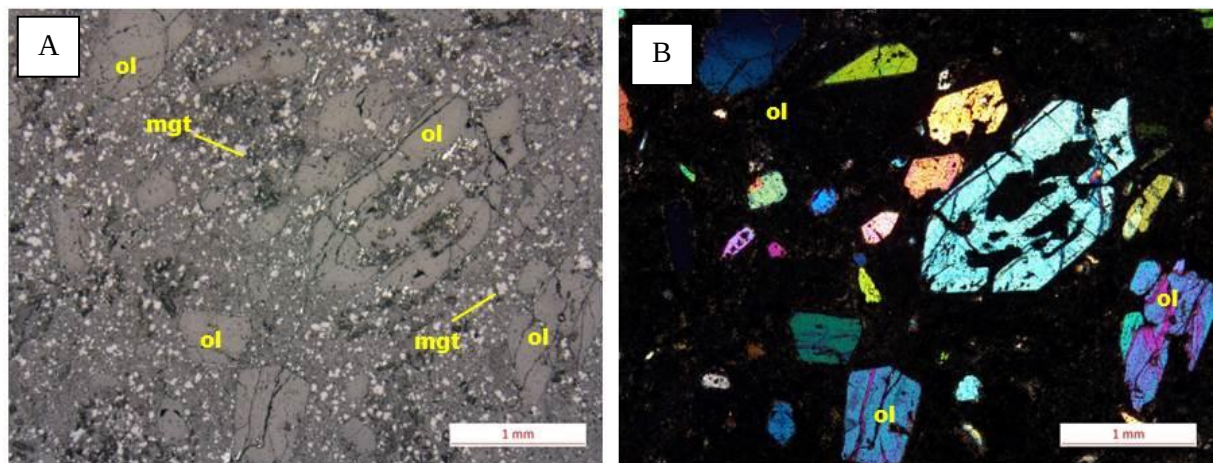


**Figure 21. WAT-1: Very fine-grained olivine melilitite. A: Reflected light photomicrograph showing abundant fine-grained titanomagnetite (mgt) in the groundmass surrounding skeletal olivine (ol). B: Cross-polarized light photomicrograph of the same location showing olivine, including a central skeletal olivine phenocryst.**

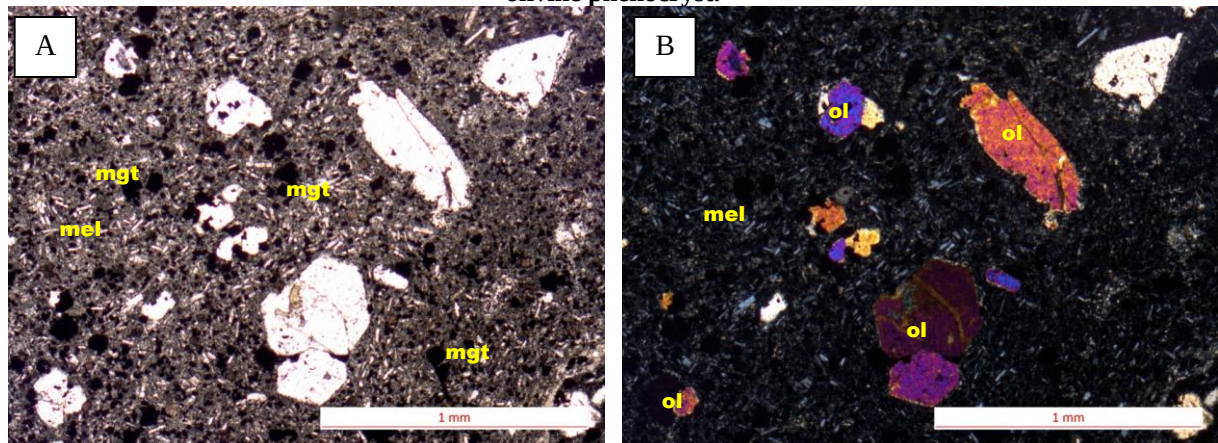


**Figure 22. BIESC-1: Very fine-grained olivine melilitite. A: transmitted light photomicrograph showing olivine phenocrysts surrounded by a matrix of opaque titanomagnetite and very fine-grained tabular melilitite. B: Cross-polarized light image of the same field of view.**

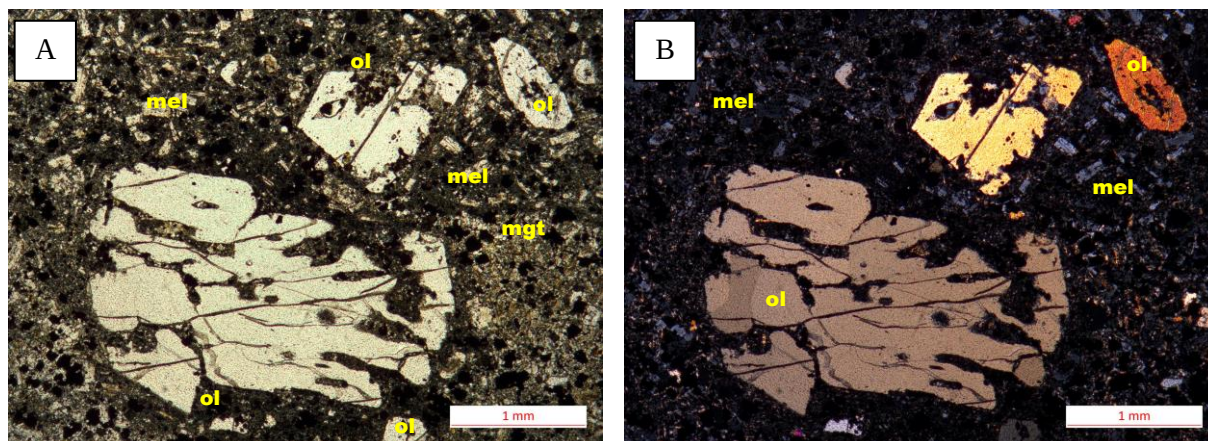


Figure 23. LOU-2: Very fine-grained olivine melilitite. A: transmitted (plane-polarised) light photomicrograph showing olivine phenocryst surrounded by a matrix of opaque titanomagnetite, fine-grained tabular melilitite and perovskite. B: the same field of view in the cross-polarised light photomicrograph. The melilitite shows first-order grey birefringence.

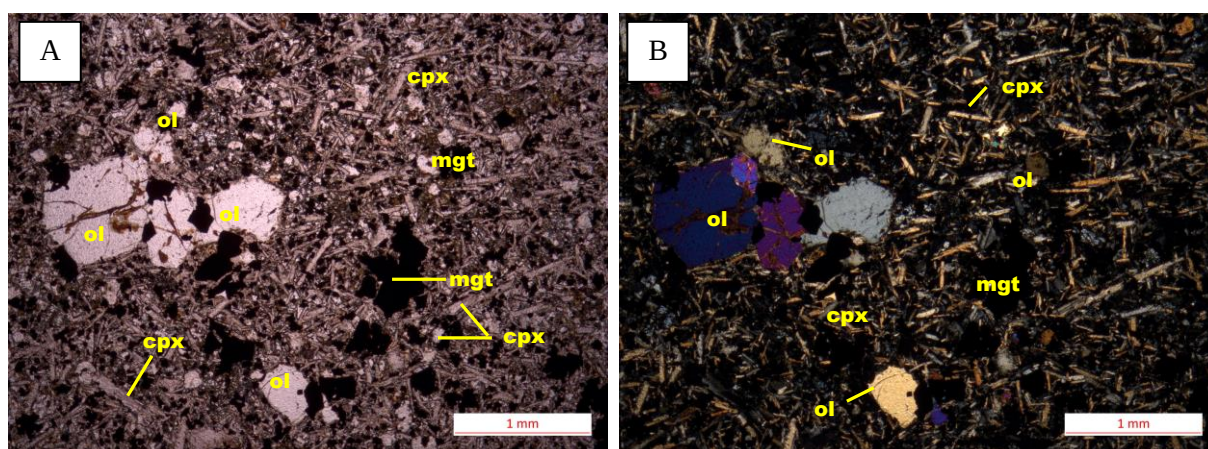


Figure 24. DSAT-2: Fine-grained nephelinite. A: transmitted (plane-polarised) light photomicrograph showing <1 mm olivine phenocrysts and olivine fragments surrounded by a matrix of fine-grained acicular clinopyroxene, opaque titanomagnetite and perovskite. B: cross-polarized light image of the same field of view. The clinopyroxene occurs as randomly oriented laths that form the majority of the groundmass.

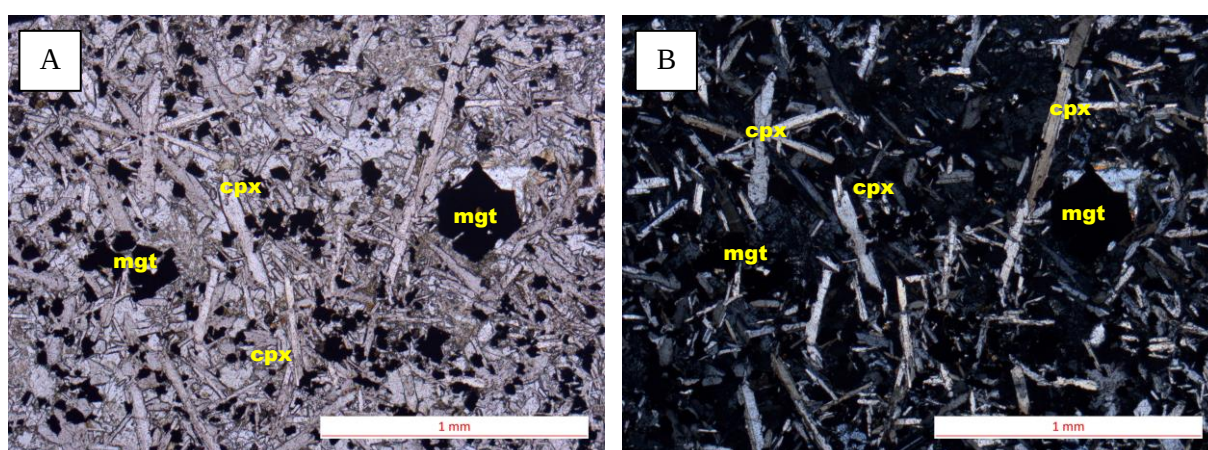


Figure 25. DSAT-3. Fine-grained nephelinite. A: Transmitted light photomicrograph showing an interlocking network of fine to medium-grained clinopyroxene laths and fine-grained opaque titanomagnetite (coarse). B: cross-polarized light image of the same field of view. The clinopyroxene occurs as randomly oriented acicular grains that form the majority of the groundmass.

#### 4.1.1 *Modal mineralogy.*

Modal abundances for the samples were determined by visual estimation from thin sections viewed microscopically at relatively low magnification (using a 2.5 x objective). Modal mineral percentage charts were used to guide estimates. The petrographic results for the Namaqualand melilitite samples are shown in Table 5 and summarized in Figure 26.

The petrographic results presented in Table 5, which is graphically illustrated in Figure 26, show that the olivine melilitites have the highest modal amounts of olivine and lowest amounts of clinopyroxene, while the olivine nephelinites have, in general, less olivine and more clinopyroxene. The olivine melilitites have a range of melilite between 10 and 30%, while the nephelinites have up to 5 % melilite. In 13 of the samples, no melilite was found. The nepheline content of the samples studied varies from 0 to 20 %. However, the olivine melilitites have a higher content of extremely fine-grained crystalline material (presumably devitrified glass), which could not be identified as any distinct mineral phase due to its fine-grained nature. The olivine nephelinites are generally coarser-grained than the olivine melilitites as they have a groundmass of inter-grown clinopyroxene needles. However, some fine-grained rocks had an indistinguishable matrix in which it was not possible to tell if nepheline or melilite were present.

All the samples contained large amounts (between 10 and 38%) of titanomagnetite and less abundant, but ubiquitous, perovskite (1 to 12 %). In only two samples was phlogopite observed: BIESA-VM1 and DSAT-1. The nephelinites were characterized as having a very low content of melilite (<10 modal % melilite) with a fine-grained matrix and clinopyroxene crystals commonly present. The nephelinites also typically had the lowest content of olivine.

Most of the samples are vesicle-free, however, two samples from the BIESA pipe were identified as vesicular during fieldwork and four vesicle-bearing samples were obtained from the DIK pipe. These samples all have the suffix "VM" and a number (e.g., BIESA-VM1). The vesicle content of the samples was excluded in the modal proportions given in Table 2 so that the vesicular and non-vesicular samples can be compared. BIESA-VM1 has a high vesicle content of ~14 % respectively. The vesicular samples also have a high degree of alteration compared to the other samples with ~30 % replacement by secondary minerals in BIESA-VM1. The vesicular melilitite sample from the DIK pipe has between 2 and 5 % vesicles and also has a high degree of alteration of between 30 to 40 % alteration into fine-grained masses of indistinguishable clay minerals.

The alteration in the non-vesicular melilitites is also variable with most samples having no detectable replacement by secondary minerals. Most of the alteration observed was the replacement of groundmass and phenocryst olivine by fine-grained clay minerals presumed to be smectites, particularly along grain boundaries and fractures. Melilite was also altered in places to fine clay minerals and it appears that alteration is mainly restricted to diffuse veins presumably around cracks and joints that provided a means of access for fluids. Most of the Namaqualand melilitites have a low degree of alteration, with mineral replacement of less than 1 %, however, two samples are more

altered: BIESD-3 (with ~17 % replacement) and ZAND-7 (with ~20 % replacement). In both of these samples, the alteration occurs primarily with the replacement of olivine phenocrysts and groundmass grains by very fine-grained clay minerals.

The term "fine-grained matrix", is a descriptive term used to describe areas of very fine-grained crystals which may represent devitrified glass or a very fine-grained assemblage of crystals. Areas of very fine-grained minerals occurring within olivine were also detected and appeared glass-like. These areas were only identified after the main microprobe work was completed, therefore, could not be analysed by microprobe in this study.

**Table 5. Estimated modal % mineralogy for the Namaqualand “melilitite” samples.**

| Pipe  | Sample Name | # | Rock Type           | Olivine | Clinopyroxene | Melilitite | Nepheline | Titanomagnetite | Perovskite | Ilmenite | Phlogopite | Fine-grained Matrix | Total | Vesicles | Alteration | MG # |
|-------|-------------|---|---------------------|---------|---------------|------------|-----------|-----------------|------------|----------|------------|---------------------|-------|----------|------------|------|
| DIK   | DIK-10      | 2 | Olivine Melilitite  | 19      | 7             | 17         | 6         | 22              | 10         | tr       | 0          | 21                  | 100   | 0        | 4          | 58   |
|       | DIK-11      | 2 | Olivine Nephelinite | 19      | 23            | 1          | 6         | 29              | 10         | 0        | 0          | 14                  | 100   | 0        | 1          | 60   |
|       | DIK-12      | 2 | Olivine Nephelinite | 28      | 3             | 2          | 2         | 32              | 3          | 0        | tr         | 31                  | 100   | 0        | 0          | 52   |
|       | DIK-13      | 1 | Olivine Nephelinite | 22      | 4             | 2          | 5         | 25              | 8          | tr       | 0          | 34                  | 100   | 0        | 0          | 48   |
|       | DIK-VM1     | 1 | Olivine Melilitite  | 16      | 32            | 12         | 12        | 25              | 3          | 0        | tr         | 0                   | 100   | 2        | 30         | 49   |
|       | DIK-VM2     | 1 | Olivine Melilitite  | 17      | 30            | 16         | 8         | 26              | 3          | 0        | 0          | 0                   | 100   | 2        | 31         | 48   |
|       | DIK-VM3     | 1 | Olivine Melilitite  | 16      | 21            | 20         | 10        | 27              | 5          | 0        | tr         | 1                   | 100   | 1        | 40         | 51   |
|       | DIK-VM4     | 1 | Olivine Melilitite  | 13      | 36            | 15         | 5         | 28              | 1          | 0        | 0          | 2                   | 100   | 5        | 30         | 57   |
| DSAT  | DSAT-1      | 1 | Nephelinite         | 1       | 46            | 0          | 14        | 36              | 2          | 0        | 1          | 0                   | 100   | 0        | 1          | 59   |
|       | DSAT-2      | 1 | Nephelinite         | 6       | 54            | 0          | 10        | 28              | 1          | 0        | tr         | 1                   | 100   | 0        | 2          | 58   |
|       | DSAT-3      | 2 | Nephelinite         | 8       | 52            | 0          | 16        | 22              | 1          | 0        | tr         | 2                   | 100   | 0        | 2          | 71   |
|       | DSAT-4      | 1 | Nephelinite         | 8       | 56            | 1          | 10        | 24              | 1          | 0        | tr         | 0                   | 100   | 0        | 1          | 51   |
| WAT   | WAT-1       | 1 | Olivine Melilitite  | 30      | 1             | 10         | 0         | 27              | 2          | 0        | 0          | 30                  | 100   | 0        | 9          | 70   |
|       | WAT-2       | 1 | Olivine Melilitite  | 33      | 1             | 11         | 0         | 26              | 1          | 0        | 0          | 28                  | 100   | 0        | 4          | 71   |
| ZAND  | ZAND-7      | 1 | Olivine Melilitite  | 16      | 20            | 20         | 1         | 25              | 7          | tr       | 0          | 11                  | 100   | 0        | 20         | 58   |
| BIESE | BIESE-1     | 1 | Nephelinite         | 8       | 55            | 0          | 10        | 25              | 2          | 0        | 0          | 0                   | 100   | 0        | 1          | 49   |
|       | BIESE-2     | 1 | Nephelinite         | 7       | 62            | 0          | 5         | 25              | 1          | 0        | tr         | 0                   | 100   | 0        | 1          | 60   |
|       | BIESE-3     | 1 | Nephelinite         | 6       | 55            | 0          | 12        | 24              | 2          | 0        | 1          | 0                   | 100   | 0        | 3          | 60   |
| BIESA | BIES-10     | 3 | Olivine Nephelinite | 16      | 32            | 0          | 5         | 28              | 5          | 0        | tr         | 15                  | 100   | 0        | 5          | 58   |
|       | BIES-11     | 2 | Olivine Nephelinite | 14      | 39            | 0          | 4         | 30              | 5          | tr       | tr         | 9                   | 100   | 0        | 5          | 58   |
|       | BIESA-1     | 1 | Olivine Nephelinite | 20      | 35            | 0          | 10        | 30              | 5          | 0        | tr         | 0                   | 100   | 1        | 5          | 58   |
|       | BIESA-2     | 1 | Olivine Nephelinite | 20      | 29            | 0          | 8         | 35              | 4          | 0        | tr         | 4                   | 100   | 0        | 5          | 58   |
|       | BIESA-VM1   | 1 | Olivine Nephelinite | 16      | 30            | 0          | 3         | 38              | 2          | 0        | 3          | 8                   | 100   | 14       | 30         | 65   |
| BIESD | BIESD-1     | 1 | Olivine Nephelinite | 10      | 35            | 0          | 15        | 35              | 3          | 0        | 0          | 2                   | 100   | Tr       | 5          | 49   |
|       | BIESD-2     | 1 | Olivine Nephelinite | 15      | 35            | 1          | 20        | 25              | 3          | 0        | 0          | 1                   | 100   | 1        | 1          | 50   |
|       | BIESD-3     | 1 | Olivine Nephelinite | 12      | 40            | 0          | 7         | 36              | 5          | 0        | 0          | 0                   | 100   | 1        | 17         | 49   |
|       | BIESD-4     | 1 | Olivine Nephelinite | 10      | 40            | 3          | 6         | 36              | 3          | 0        | 0          | 2                   | 100   | 3        | 6          | 50   |
| BIESB | BIESB-1     | 1 | Olivine Melilitite  | 30      | 13            | 15         | 10        | 30              | 2          | 0        | tr         | 0                   | 100   | 0        | 0          | 64   |
|       | BIESB-2     | 1 | Olivine Melilitite  | 28      | 10            | 20         | 12        | 20              | 5          | 0        | 0          | 5                   | 100   | 0        | 1          | 62   |
|       | BIESB-3     | 1 | Olivine Melilitite  | 32      | 3             | 15         | 5         | 30              | 3          | 0        | 0          | 12                  | 100   | 0        | 1          | 60   |
| BIESC | BIESC-1     | 1 | Olivine Melilitite  | 25      | 3             | 18         | 1         | 25              | 2          | 0        | 0          | 26                  | 100   | 0        | 1          | 62   |
|       | BIESC-2     | 1 | Olivine Melilitite  | 25      | 12            | 12         | 6         | 22              | 2          | 0        | 0          | 21                  | 100   | 0        | 5          | 50   |
|       | BIESC-3     | 1 | Olivine Melilitite  | 20      | 4             | 12         | 2         | 35              | 2          | 0        | tr         | 25                  | 100   | 0        | 0          | 50   |
| LOU   | LOU-2       | 1 | Olivine Melilitite  | 15      | 5             | 25         | 5         | 30              | 5          | 0        | 0          | 15                  | 100   | 0        | 0          | 57   |
|       | LOU-3       | 1 | Olivine Melilitite  | 16      | 1             | 30         | 4         | 26              | 3          | tr       | 0          | 20                  | 100   | 0        | 0          | 59   |
|       | LOU-4       | 1 | Olivine Melilitite  | 12      | 15            | 25         | 5         | 23              | 5          | 0        | tr         | 15                  | 100   | 0        | 0          | 58   |

# Number of thin sections examined

\* Fine-grained matrix refers to extremely fine-grained areas of the thin sections where the small mineral grain size makes any meaningful estimate of modal proportions impossible.

\*\*"tr" refers to less than 1% abundance and is assumed to be negligible.

\*\*\* "0" not observed and assumed to be negligible.

Rock-type classification using Moore 1979 and Le Maitre, 2002.

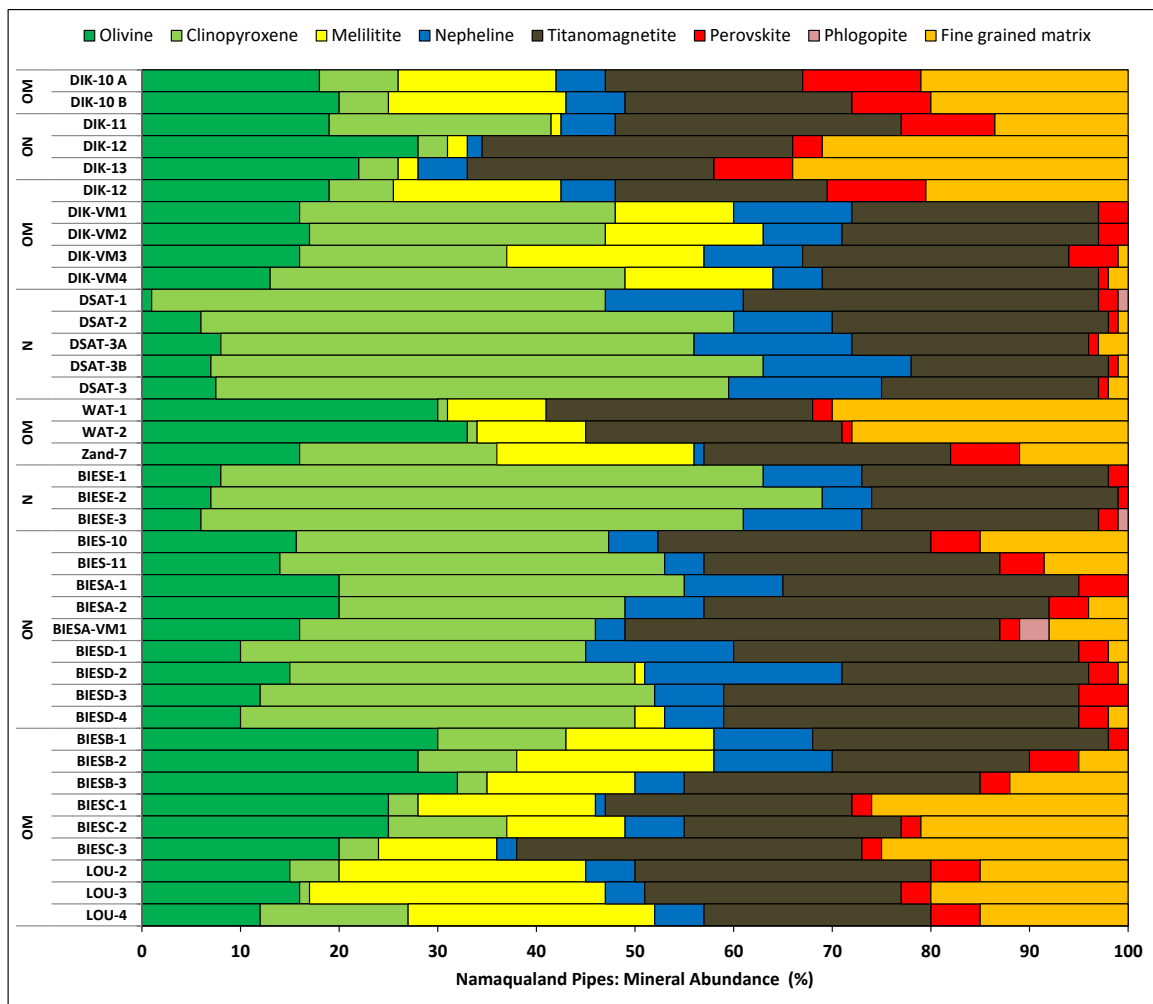


Figure 26. Modal mineralogy of the Namaqualand magmatic pipes compared.

The modal mineralogy results for the Namaqualand melilitites are further compared in Figure 27. Figure 27A shows that the nephelinites have the highest clinopyroxene content and this decreases in the olivine nephelinites and is lowest in the olivine melilitites. Olivine, on the other hand, increases in average modal abundance from the nephelinites to the olivine melilitites. Thus, there is a strong negative relationship between clinopyroxene and olivine in the Namaqualand samples, and a weaker negative correlation between clinopyroxene and melilite (Figure 27B). The relationship between nepheline and olivine content of the Namaqualand samples, illustrated in Figure 27C, shows an even weaker negative correlation, with the nephelinites having the highest average nepheline content while the olivine melilitites, on average, have the lowest.

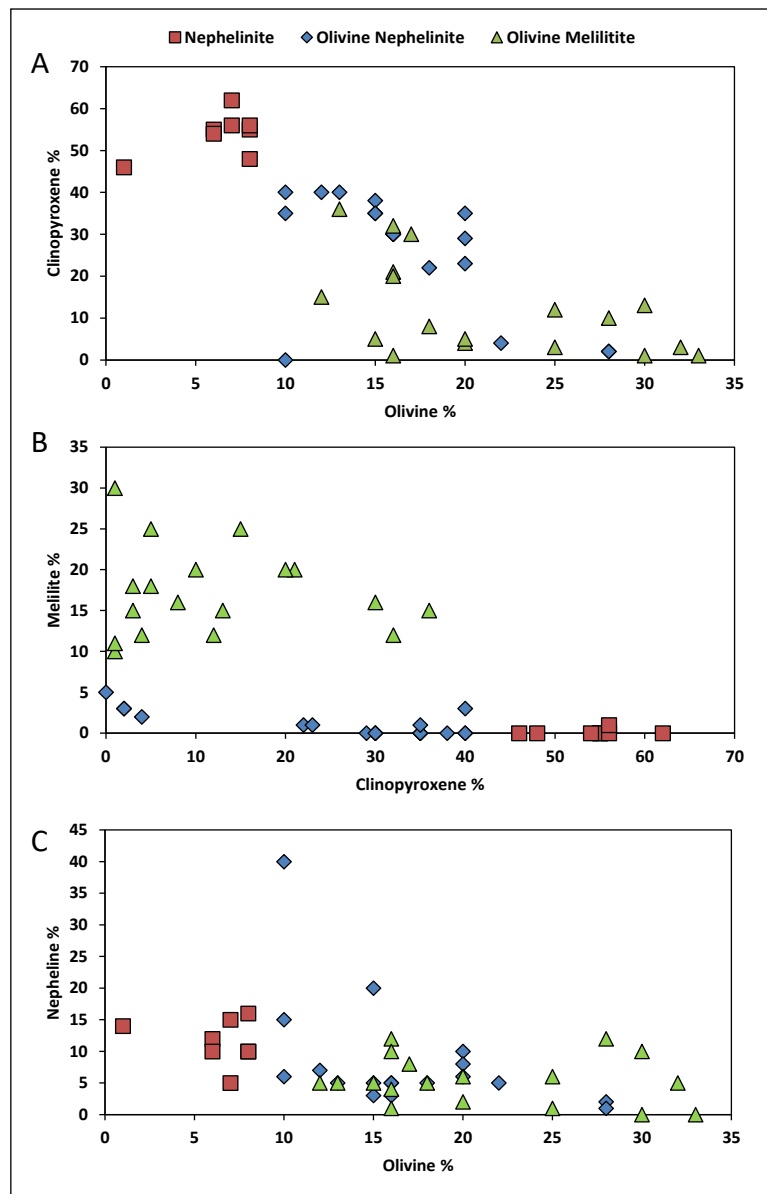


**Figure 27. Plots of the modal mineral content of the main phases in the Namaqualand "melilitites". (a) Olivine vs. clinopyroxene within the Namaqualand melilitites. (b) Melilite versus clinopyroxene modal abundance. (c) Nepheline vs. olivine modal abundance.**

To quantify the precision of the above modal percentage estimates, accounting for both possible bias in estimation and natural lithological/textural variability of the igneous rock samples, replicate modal percentages were estimated for sets of two to three thin sections made from different parts of the same sample. A comparison of the results for these replicate estimates (shown in Table 6) indicates that estimated modal proportions for the vast majority of minerals in the samples are similar within a relative standard deviation of about 30%. The greatest differences observed were for sample DSAT3 which showed a relatively large difference in a small abundance of devitrified glass (1 vs. 3 %).

**Table 6. Comparison of visually estimated mineral proportions for replicate thin sections from the Namaqualand melilitite pipes.**

| Sample Name                 | Olivine | Clinopyroxene | Melilitite | Nepheline | Titanomagnetite | Perovskite | Fine-grained matrix | Total |
|-----------------------------|---------|---------------|------------|-----------|-----------------|------------|---------------------|-------|
| BIES-10A                    | 16      | 30            | 0          | 5         | 30              | 5          | 14                  | 100   |
| BIES-10B                    | 15      | 35            | 0          | 5         | 27              | 5          | 13                  | 100   |
| BIES-10B                    | 15      | 35            | 0          | 5         | 27              | 5          | 13                  | 100   |
| Difference                  | 1       | 5             | 0          | 0         | 3               | 0          | 1                   |       |
| Rel. standard deviation (%) | 3       | 7             | -          | 0         | 5               | 0          | 4                   |       |
| BIES-11A                    | 13      | 40            | 0          | 5         | 30              | 5          | 7                   | 100   |
| BIES-11B                    | 15      | 38            | 0          | 3         | 30              | 4          | 10                  | 100   |
| Difference                  | 2       | 2             | 0          | 2         | 0               | 1          | 3                   |       |
| Rel. standard deviation (%) | 7       | 3             | -          | 25        | 0               | 11         | 18                  |       |
| DIK-10A                     | 18      | 8             | 16         | 5         | 20              | 12         | 21                  | 100   |
| DIK-10B                     | 20      | 5             | 18         | 6         | 23              | 8          | 20                  | 100   |
| Difference                  | 2       | 3             | 2          | 1         | 3               | 4          | 1                   |       |
| Rel. standard deviation (%) | 5       | 23            | 6          | 9         | 7               | 20         | 2                   |       |
| DIK-11A                     | 18      | 22            | 1          | 5         | 30              | 9          | 15                  | 100   |
| DIK-11B                     | 20      | 23            | 1          | 6         | 28              | 10         | 12                  | 100   |
| Difference                  | 2       | 1             | 0          | 1         | 2               | 1          | 3                   |       |
| Rel. standard deviation (%) | 5       | 2             | 0          | 9         | 3               | 5          | 11                  |       |
| DIK-12A                     | 28      | 3             | 2          | 2         | 32              | 3          | 30                  | 100   |
| DIK-12B                     | 28      | 3             | 2          | 1         | 31              | 3          | 32                  | 100   |
| Difference                  | 0       | 0             | 0          | 1         | 1               | 0          | 2                   |       |
| Rel. standard deviation (%) | 0       | 0             | 0          | 33        | 2               | 0          | 3                   |       |
| DSAT-3A                     | 8       | 48            | 0          | 16        | 24              | 1          | 3                   | 100   |
| DSAT-3B                     | 7       | 56            | 0          | 15        | 20              | 1          | 1                   | 100   |
| Difference                  | 1       | 8             | 0          | 1         | 4               | 0          | 2                   |       |
| Rel. standard deviation (%) | 7       | 8             | -          | 3         | 9               | 0          | 50                  |       |

## 4.2. Petrographic Comparison of Namaqualand and Bushmanland Melilitites.

For comparative purposes, modal percentages of some samples from the Bushmanland melilitite pipes were also estimated and these are provided in Table 7. These samples were all collected by P. Janney for a companion study. The samples studied were mostly olivine nephelinites (17) with a smaller number of olivine melilitites (4). These samples had more consistent abundances of olivine (20 to 40 %) but more variable clinopyroxene (0 to 38 %), ubiquitous titanomagnetite (15-30 %), variable perovskite (1 to 15%) and highly variable percentages of extremely fine-grained crystalline matrix (0-50%) that likely represents devitrified glass, or, in the case of HOD-5, fibrous clinopyroxene.

**Table 7: Modal mineralogy of the Bushmanland samples examined for comparative purposes.**

| Sample Name | Rock Type           | Alteration        | Matrix         | Olivine | Clinopyroxene | Melilitite | Nepheline | Titanomagnetite | Perovskite | Ilmenite | Phlogopite | Fine-grained matrix | Total | Alteration/Clay | Vesicles | Mg # |
|-------------|---------------------|-------------------|----------------|---------|---------------|------------|-----------|-----------------|------------|----------|------------|---------------------|-------|-----------------|----------|------|
| WK-1        | Olivine Nephelinite | Partially Altered | Fine-grained   | 36      | 1             | 5          | 1         | 27              | 13         | Tr       | 0          | 17                  | 100   | 5               | 0        | 71   |
| WKR-1       | Olivine Nephelinite | Fresh             | V fine-grained | 31      | 30            | 0          | 1         | 20              | 8          | 0        | 0          | 10                  | 100   | 0               | 0        | 70   |
| WKR-2       | Olivine Melilitite  | Partially Altered | V-fine-grained | 35      | 1             | 18         | 1         | 15              | 15         | Tr       | 0          | 15                  | 100   | 5               | 0        | 70   |
| WKR-3       | Olivine Melilitite  | Fresh             | V-fine-grained | 35      | 5             | 10         | 1         | 20              | 15         | Tr       | 0          | 14                  | 100   | 0               | 0        | 70   |
| WKSAT2-2    | Olivine Nephelinite | Fresh             | V-fine-grained | 30      | 5             | 1          | 0         | 20              | 15         | Tr       | 0          | 29                  | 100   | 0               | 0        | 71   |
| WKSAT3-1    | Olivine Nephelinite | Partially Altered | V-fine-grained | 34      | 2             | 0          | 0         | 25              | 9          | Tr       | 0          | 30                  | 100   | 5               | 0        | 73   |
| Jen-5       | Olivine Melilitite  | Fresh             | Fine-grained   | 28      | 15            | 7          | 1         | 28              | 8          | 0        | 0          | 13                  | 100   | 0               | 1        | 72   |
| Gill-5      | Olivine Nephelinite | Altered           | V-fine-grained | 30      | 14            | 0          | 0         | 25              | 10         | 0        | 0          | 21                  | 100   | 10              | 0        | 71   |
| BKA-10      | Olivine Nephelinite | Fresh             | V-fine-grained | 30      | 5             | 0          | 0         | 20              | 15         | Tr       | 0          | 30                  | 100   | 0               | 0        | 70   |
| BKA-11      | Olivine Nephelinite | Fresh             | V-fine-grained | 30      | 15            | 0          | 1         | 20              | 10         | Tr       | 0          | 24                  | 100   | 0               | 0        | 72   |
| BKB-10      | Olivine Nephelinite | Fresh             | V-fine-grained | 24      | 35            | 0          | 5         | 18              | 8          | Tr       | 5          | 5                   | 100   | 0               | 0        | 74   |
| BKB-11      | Olivine Nephelinite | Partially Altered | Fine-grained   | 23      | 35            | 1          | 5         | 25              | 8          | 0        | 3          | 0                   | 100   | 2               | 0        | 74   |
| GMPA-1      | Olivine Nephelinite | Partially Altered | V-fine-grained | 38      | 10            | 1          | 0         | 28              | 1          | 0        | 0          | 22                  | 100   | 1               | 0        | 74   |
| GMPAX-1     | Olivine Nephelinite | Partially Altered | V-fine-grained | 35      | 35            | 1          | 1         | 20              | 8          | 0        | 0          | 0                   | 100   | 2               | 0        | 74   |
| ZH-1        | Olivine Nephelinite | Partially Altered | V-fine-grained | 35      | 6             | 0          | 1         | 20              | 8          | 0        | 0          | 30                  | 100   | 2               | 0        | 71   |
| ZWR1-1      | Olivine Nephelinite | Partially Altered | V-fine-grained | 37      | 10            | 0          | 2         | 30              | 6          | 0        | 0          | 15                  | 100   | 3               | 1        | 71   |
| ZWR2-2      | Olivine Nephelinite | Partially Altered | Fine-grained   | 23      | 30            | 1          | 1         | 28              | 8          | 0        | 0          | 9                   | 100   | 1               | 0        | 74   |
| ZWR2-3      | Olivine Nephelinite | Fresh             | Fine-grained   | 28      | 33            | 0          | 1         | 25              | 8          | 0        | 0          | 5                   | 100   | 0               | 0        | 77   |
| SP-3        | Olivine Nephelinite | Partially Altered | Fine-grained   | 28      | 33            | 1          | 1         | 18              | 10         | 0        | 5          | 4                   | 100   | 1               | 0        | 73   |
| HO-4        | Olivine Nephelinite | Fresh             | V-fine-grained | 21      | 1             | 0          | 0         | 27              | 2          | 0        | 5          | 44                  | 100   | 0               | 0        | 77   |
| HO-5        | Olivine Nephelinite | Fresh             | V-fine-grained | 25      | 0             | 0          | 0         | 20              | 1          | 0        | 4          | 50                  | 100   | 0               | 0        | 77   |

\* Fine-grained matrix refers to extremely fine-grained areas of the thin sections where the small mineral grain size makes any meaningful estimate of modal proportions impossible.

Tr = less than 1 modal % of a mineral observed.

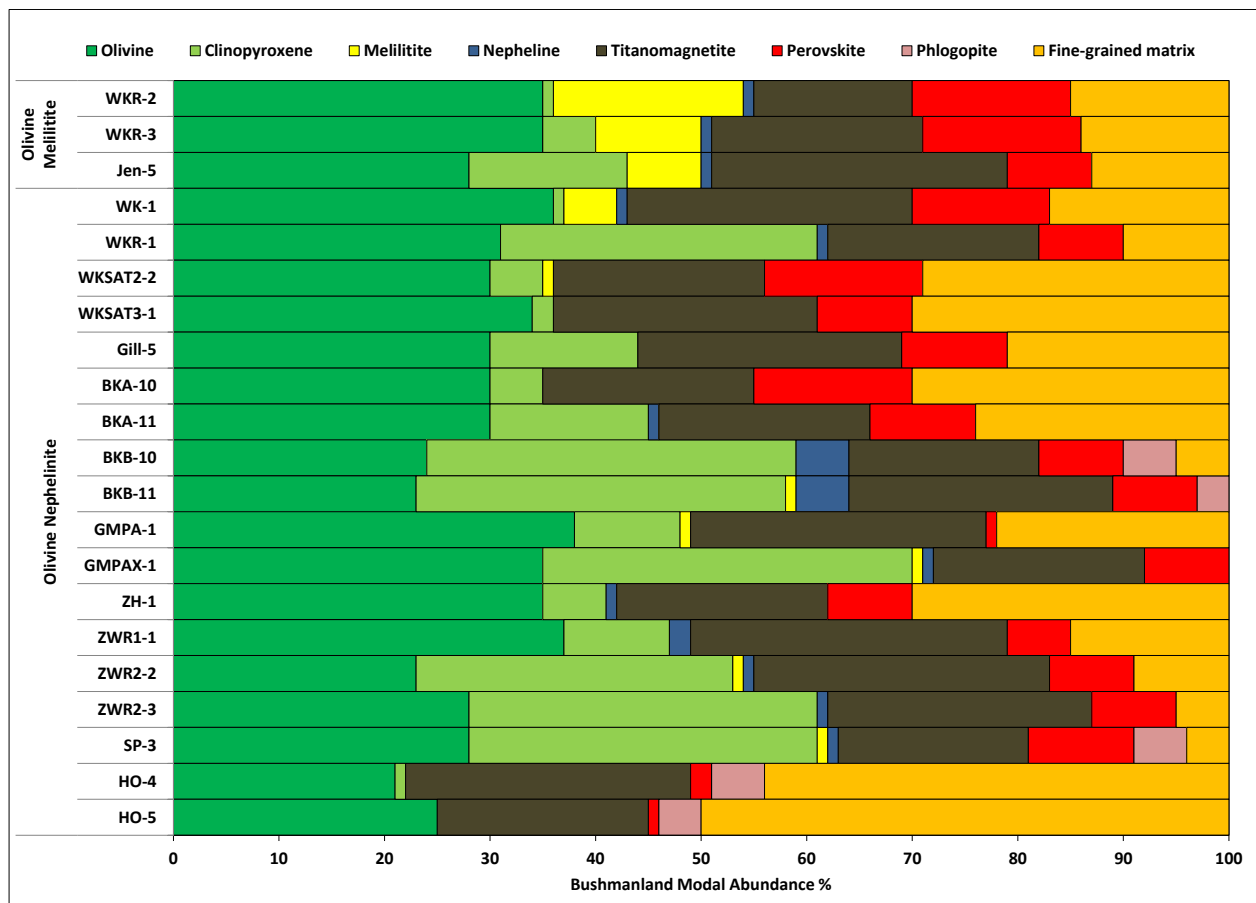


Figure 28: Modal data for the Bushmanland ‘melilitite’ samples presented graphically.

### 4.3. Petrographic classification by modal mineralogy.

The Namaqualand and Bushmanland modal mineralogy results were used to compare and classify the melilitite samples and these results are provided in Figure 29. The figure shows a ternary plot of the Namaqualand and Bushmanland melilitite sample’s modal melilitite, clinopyroxene and olivine content normalized to 100 %. The diagram has been modified after Le Bas and Streckeisen, 1991. The results indicate, that using this method, the samples are classified as olivine melilitites or olivine nephelinites/ultramafic volcanics. However, none were classified as melilitites due to the predominating presence of olivine and/or clinopyroxene >10%.

In comparison between the Namaqualand and Bushmanland samples, it is observed that the Namaqualand samples have a significantly higher proportion of melilitite and clinopyroxene in their modal mineralogy while the Bushmanland samples have a much greater proportion of olivine in their modal mineralogy. This results in more *sensu stricto* olivine melilitites (17 of 37 samples), fewer olivine nephelinites (13 of 37 samples) and nephelinites (3 of 37 samples) within the Namaqualand pipes studied while the Bushmanland pipes studied were mostly olivine nephelinites (18 of 21 samples) with only a few olivine melilitites (3 of 21 samples).

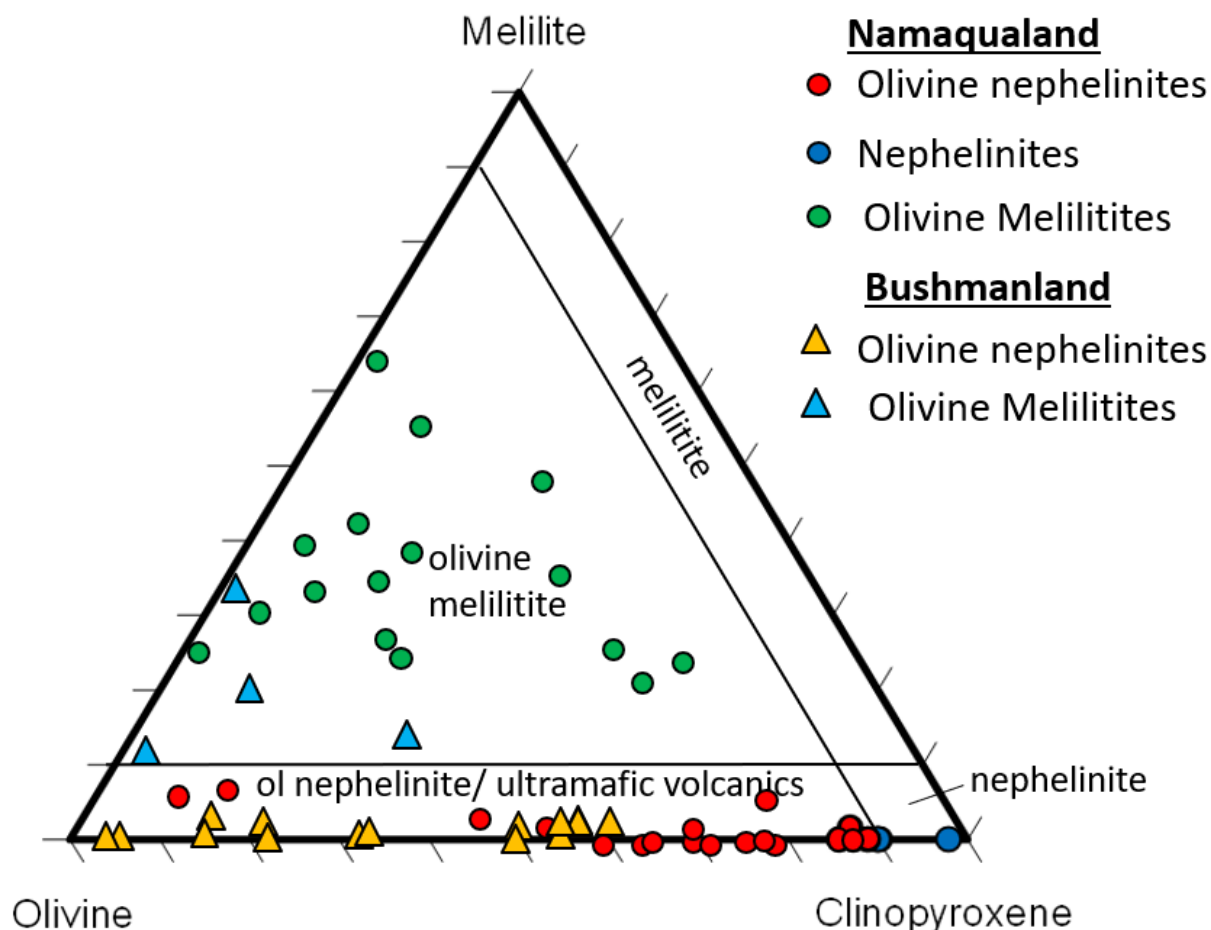


Figure 29. Classification diagram for the Namaqualand and Bushmanland “melilitite” samples based on normalised modal content of olivine, clinopyroxene and melilite for the different samples, which is plotted to classify the rocks using the technique by Le Bas and Streckeisen (1991).

#### 4.4. Namaqualand Country rock samples:

Samples of crystalline country rock were obtained in proximity to most of the Namaqualand melilitite pipes sampled. These are meant to be representative of the upper crustal country rock surrounding the melilitite pipes. These samples permit the mineralogy and geochemistry of the rocks into which the pipes intruded to be characterised and to aid in determining if contamination by the upper crust played a role in their petrogenesis. The upper crustal basement rocks surrounding the Namaqualand melilitite pipes are either Rietpoort Granite of the Early Cretaceous Koegel Fontein Igneous Complex (all pipes on Farm Biesiesfontein; e.g., Curtis *et al.*, 2011) or mid-Proterozoic gneisses of the Garies Terrane of the Namaqualand Metamorphic Complex (Hartnady *et al.*, 1985; Eglington, 2006; Viola *et al.*, 2012). The mineral abundances of the country rock samples are provided (Table 8) where a rock name is provided for each of the country rock samples. Whole-rock geochemical data for these samples are also provided (Appendix D).

**Table 8: Estimated modal mineralogy of the Namaqualand country rock samples.**

| Grain size     | Rock type               | Related Pipe* | Sample name | Alkali feldspar | Plagioclase | Quartz | Opakes | Amphibole | Clays/ Chlorite | Biotite/ muscovite | Clinopyroxene | Total |
|----------------|-------------------------|---------------|-------------|-----------------|-------------|--------|--------|-----------|-----------------|--------------------|---------------|-------|
| Medium-grained | Granitic gneiss         | DIK           | RTPT-1      | 60              | 0           | 25     | Tr     | 10        | 0               | 5                  | Tr            | 100   |
| Medium-grained | Granitic gneiss         | DIK           | DIK-CR1     | 50              | -           | 40     | 1      | 0         | 9               | Tr                 | -             | 100   |
| Medium-grained | Granitic gneiss         | DSAT          | DSAT-CR1    | 50              | 0           | 45     | Tr     | 0         | 3               | 2                  | Tr            | 100   |
| Coarse-grained | Granitic gneiss         | WAT           | WAT CR1     | 30              | 0           | 40     | 1      | 0         | 28              | 1                  | 0             | 100   |
| Medium-grained | Banded amphibole gneiss |               | WAT CR2     | 0               | 35          | 0      | 5      | 35        | 14              | 1                  | 10            | 100   |
| Medium-grained | Granite                 | BIESA         | BIESA-CR1   | 12              | 0           | 40     | 2      | 0         | 41              | 5                  | 0             | 100   |
| Fine-grained   | Granophyre              | BIESD         | BIESD-CR1   | 22              | 0           | 45     | 2      | 1         | 30              | 0                  | 0             | 100   |
| Medium-grained | Granophyre              |               | BIESD-CR2   | 13              | -           | 45     | 1      | 1         | 40              | Tr                 | 0             | 100   |
| Fine-grained   | Meta basalt             | LOU           | LOU-1       | -               | -           | 1      | 10     | 70        | 18              | 0                  | 1             | 100   |
| Coarse-grained | Granitic gneiss         |               | LOU-CR-1    | 35              | 0           | 42     | Tr     | 2         | 20              | 1                  | 0             | 100   |

\*DIK (Dikdoorn), DSAT (Dikdoorn Satellite), WAT (Watervaal), BIES (Biesiesfontein), LOU (Louisfontein).

## 4.5. Mineral chemistry Results:

The mineral chemistry data is based on electron microprobe analysis of thin sections from the following samples: WAT-1, DSAT-2, LOU-3 and BIESE-1. This was done in order to identify and determine the chemical compositions of the main phenocryst minerals present to determine the mineral compositional variability in the Namaqualand cluster from within a few samples for comparison with other studies. These were selected as they represented a range of whole rock compositions. The main minerals analysed were olivine, melilite, titanomagnetite, perovskite and phlogopite.

Some data collected for minerals from previous studies of the Namaqualand and Bushmanland melilitites (particularly Dikdoorn and Zandkopsdrift) were reported by Moore (1979), Moore and Erlank (1979), Haggerty *et al.* (1985) and Boctor and Yoder (1983). These mineral data are provided for comparison in the diagrams illustrating variations in mineral compositions.

### 4.5.1 Olivine Mineral Chemistry:

The olivine mineral chemistry data for the Namaqualand olivine melilitites from this study, (Appendix X) and other sources, shows that the Namaqualand melilitites from this study have an average Mg number of  $81.2 \pm 2.6$ , while the historical Namaqualand melilitites have an Mg number of  $81.4 \pm 2.5$ . The Bushmanland olivine grains are more primitive with an average Mg number of  $84.7 \pm 3.6$ . The combined data collected for the Namaqualand and Bushmanland regions (Figure 30) shows that the olivine melilitites have olivine grains with Mg numbers between the lowest of ~67 and the highest of ~92 with an average for the data from both clusters at  $82.5 \pm 3.3$ .

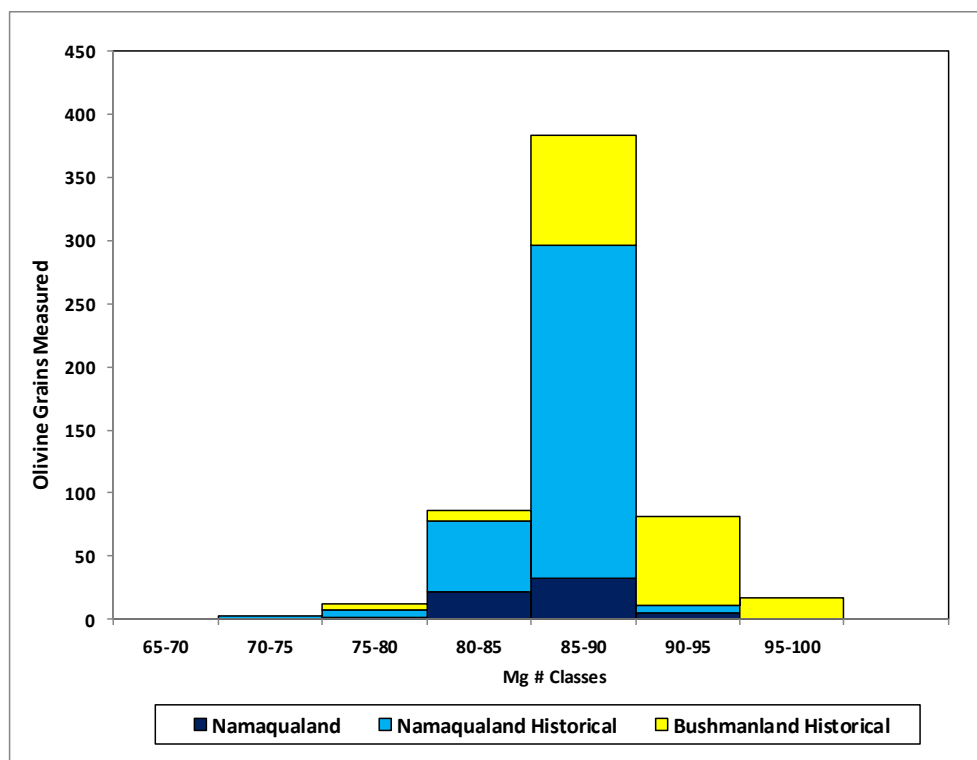


**Figure 30: Mineral chemistry data comparison for the Namaqualand and Bushmanland melilitites. The Namaqualand and Bushmanland historical data were obtained from Moore 1979 and Boctor and Yoder (1983).**

A compilation of the olivine mineral chemistry data from this study, as well as the data from previous studies by Moore 1979 and Boctor and Yoder (1983), shows a distinct positive correlation in Ni vs. MgO for the olivine grains of the Bushmanland and Namaqualand regions. Historical Bushmanland data show the highest Ni and MgO values, however, there is some overlap between the two clusters. The data is presented in Figure 31 and shows a positive correlation of Ni with MgO for the samples from Namaqualand.

For the data from this study, the olivine grains from the same cluster tend to have similar compositions with the olivines from WAT-1 and LOU-3 having the highest Ni and MgO values, while the samples from BIESE-1 have the lowest Ni and MgO olivines. The olivines from DSAT-2 intermediate while those from ZAND-7 range between low to intermediate in Ni and MgO when compared to the other samples.

A compilation of all the olivine analysis from the four Namaqualand samples selected for mineral analysis is provided in Figure 32 which shows an overlap in the Mg # of the core and rims of the olivine grains, therefore, no resolvable separation between cores and rims on the basis of Mg# from the data that was collected.

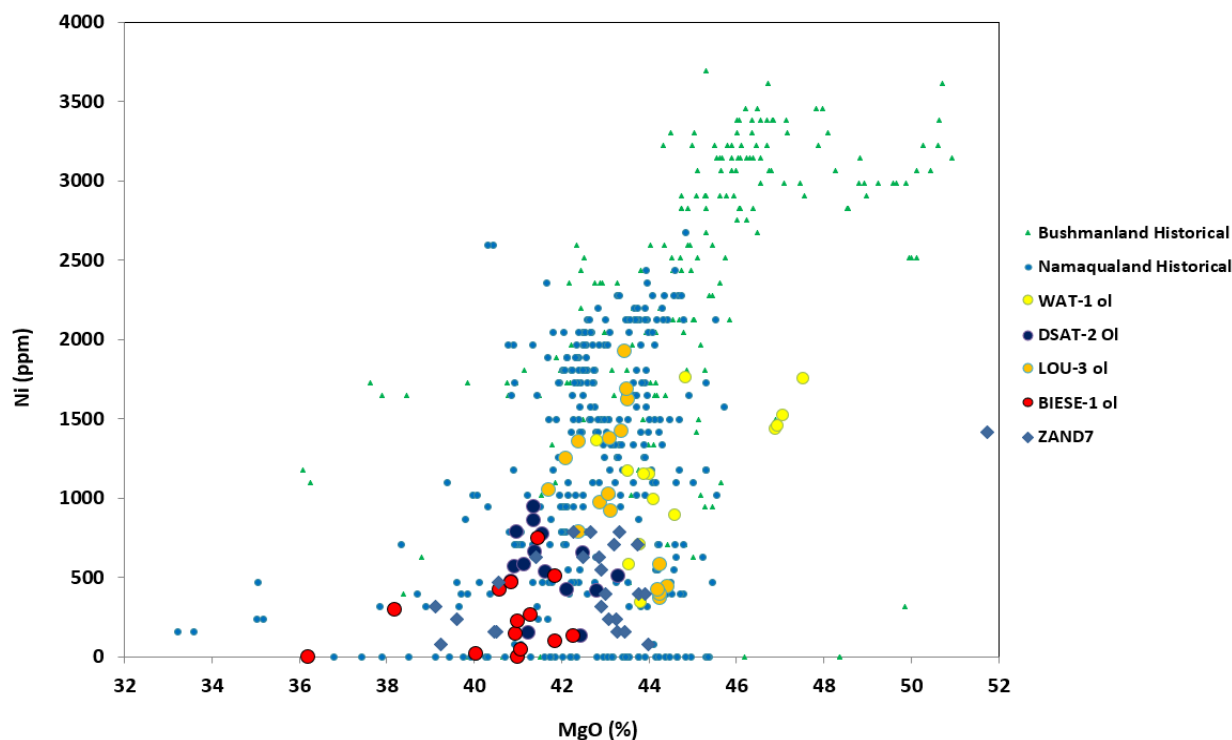


Figure 31. Combined MgO vs. Ni data for this study as well as the study by Moore (1979) and Boctor and Yoder (1983).

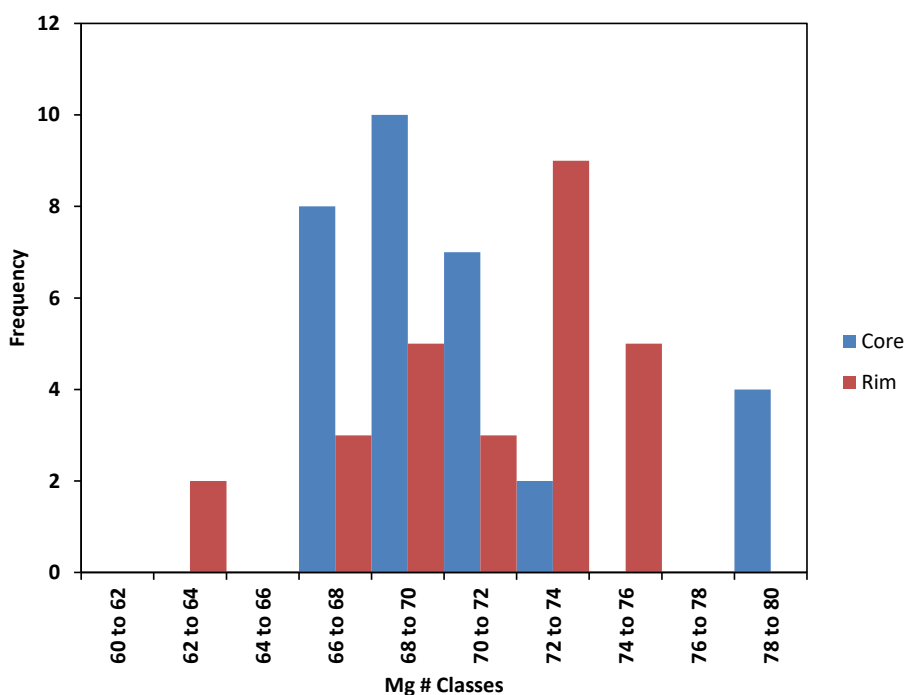


Figure 32. Combined probe results for all olivine grains showing Mg number of cores and rims.

#### 4.5.2 *Fe-Oxide Mineral Chemistry:*

The electron microprobe results for titaniferous magnetite (Appendix B) are illustrated in Figure 33, which shows the MgO content plotted against MnO and TiO<sub>2</sub>. The data include those from the four

samples analysed in this study as well as data from Haggerty *et al.* (1985), Moore (1979) and Boctor and Yoder (1983). The data indicates that there is a broad clustering of data with no clear trend in the data for either MgO vs MnO or MgO vs TiO<sub>2</sub>. However, for the samples collected for DSAT-2, there appears to be a slight negative trend for MgO values vs MnO and MgO vs TiO<sub>2</sub> which could indicate the influence of magma differentiation during crystallization.

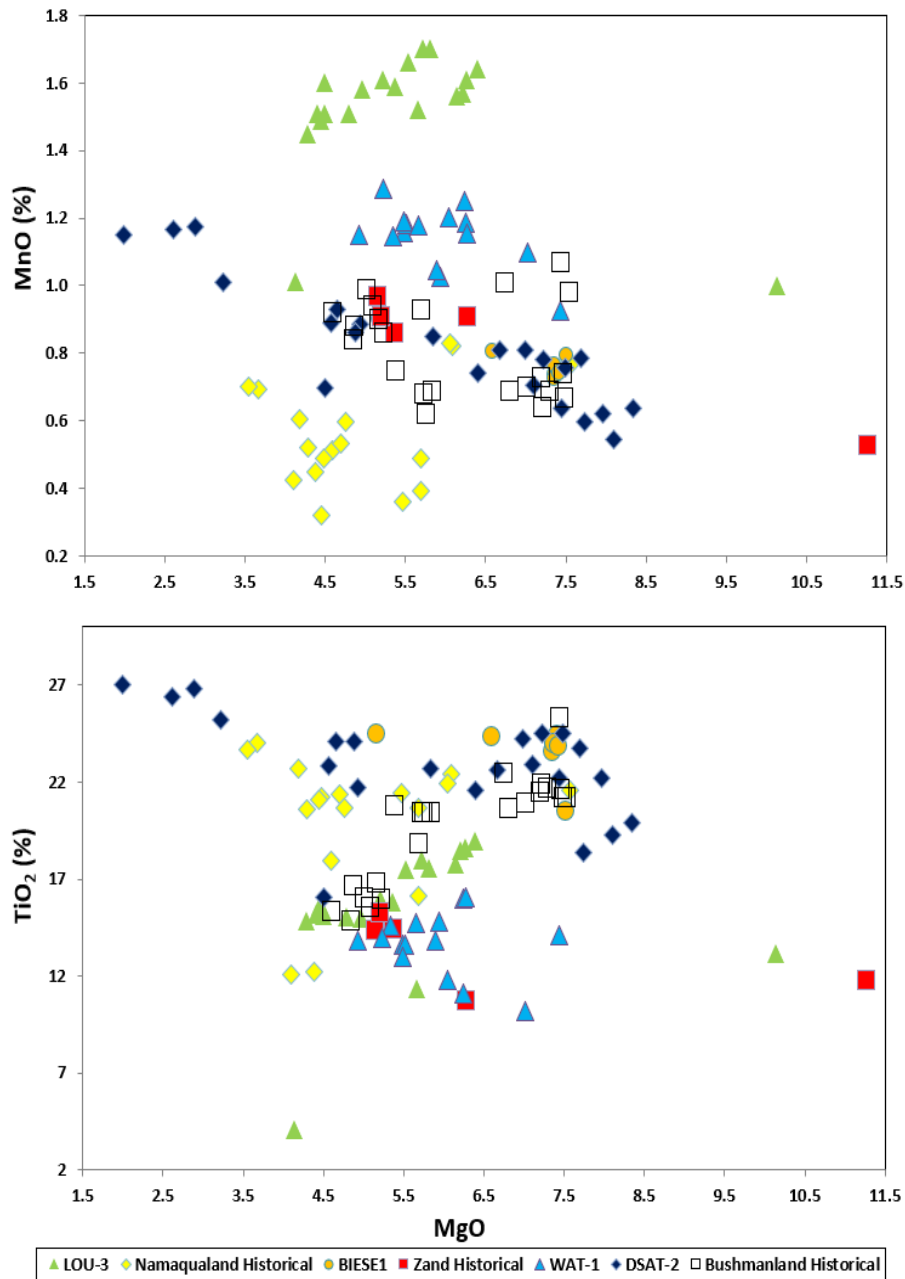


**Figure 33: Mineral chemistry data for Fe-oxide (titanomagnetite) grains from the Namaqualand melilitites compared to data from other studies. The Zand data was obtained from Boctor and Yoder (1986). The Namaqualand historical data is from Moore (1979) and Boctor and Yoder (1983). The historical data from Bushmanland was obtained from Haggerty *et al.* (1985).**

## 5. ELEMENTAL AND ISOTOPE GEOCHEMISTRY:

The geochemical results for the Namaqualand melilitite pipes include major element and trace element data for 36 whole rock samples as well as radiogenic isotope analysis of 22 samples. It is important to re-emphasise that the sampled igneous rocks are referred to here as "melilitites" (*sensu lato*) even though some of the samples have less than <10 modal percent melilite, and so do not fit the strict definition of melilitites or olivine melilitites.

### 5.1.1 *Namaqualand melilitite samples.*

The Namaqualand olivine melilitite major element compositions are provided in Appendix D. Compared to less silica-undersaturated igneous rock types, such as alkali basalts and basanites, the melilitites have low SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and relatively high TiO<sub>2</sub>, FeO<sup>tot</sup> and CaO. However, MgO, Na<sub>2</sub>O and K<sub>2</sub>O contents span relatively wide ranges from 8 to 17 wt. %, 0.8 to 2.6 wt. % and 1.3 to 2.3 wt. %, respectively.

The vast majority of the melilitite samples are non-vesicular and fresh to mildly altered, having typically been collected from the central portion of the melilitite pipes. A few of the samples are vesicular melilitite specimens obtained from the margins of the melilitite pipes. These are generally more highly altered than the non-vesicular samples but, in most cases, the vesicular and non-vesicular melilitite samples are chemically similar.

### 5.1.2 *Country rock samples.*

The eight country rock samples analysed derive from granites of the Koegel Fontein complex (BIESA-CR1, BIESD-CR1, BIESD-CR2 and RTPT-1) and Bushmanland gneisses surrounding the Louisfontein, Waterval, Dikdoorn and Dikdoorn Satellite pipes (LOU-CR1, WAT-CR1, WAT-CR2, DIK-CR1, DSAT-CR1). Most of these samples have similar compositions with high SiO<sub>2</sub> (of  $\approx$  75 wt. %), Al<sub>2</sub>O<sub>3</sub> (of 12-15 wt. %) and K<sub>2</sub>O (4.7 to 6.9). The samples also have low Fe<sub>2</sub>O<sub>3</sub> (1.5 to 2.9 wt. %), MgO (0.1 to 0.4 wt. %) and CaO (0.2 to 1.4 wt. %). One amphibole-rich gneiss sample (WAT-CR2; representing the melanocratic portion of a banded gneiss) has much lower SiO<sub>2</sub> (49.2) and higher Fe<sub>2</sub>O<sub>3</sub> and MgO (10.3 and 7.3 wt. %, respectively) than the other gneiss samples. The most likely reason for this is that WAT-CR1 and WAT-CR2 are the leucocratic and melanocratic bands of a single-banded gneiss (with banding on the scale of 0.25-0.5 m). So, the average composition of the whole gneiss is intermediate between these two.

## 5.2. Rock classification.

### 5.2.1 Geochemical criteria.

The samples can be classified by their major element compositions using the total alkalis vs. silica (TAS) diagram of Le Maitre *et al.* (1989). The TAS diagram shown in Figure 34 shows that the Namaqualand olivine melilitites fall to the low  $\text{SiO}_2$  side of the picrobasalt and basanite field. The samples have  $\text{SiO}_2$  values of between 30 and 38 % while  $\text{Na}_2\text{O} + \text{K}_2\text{O}$  is between ~1.5 and 5.5 %. The data plotted were normalized to volatile-free so that all major oxides sum up to 100 wt. % in order to remove any inter-sample variations caused by variations in volatile content. According to this diagram the rocks are classified as foidites, which indicates further classification or alternative methods of classification are needed.

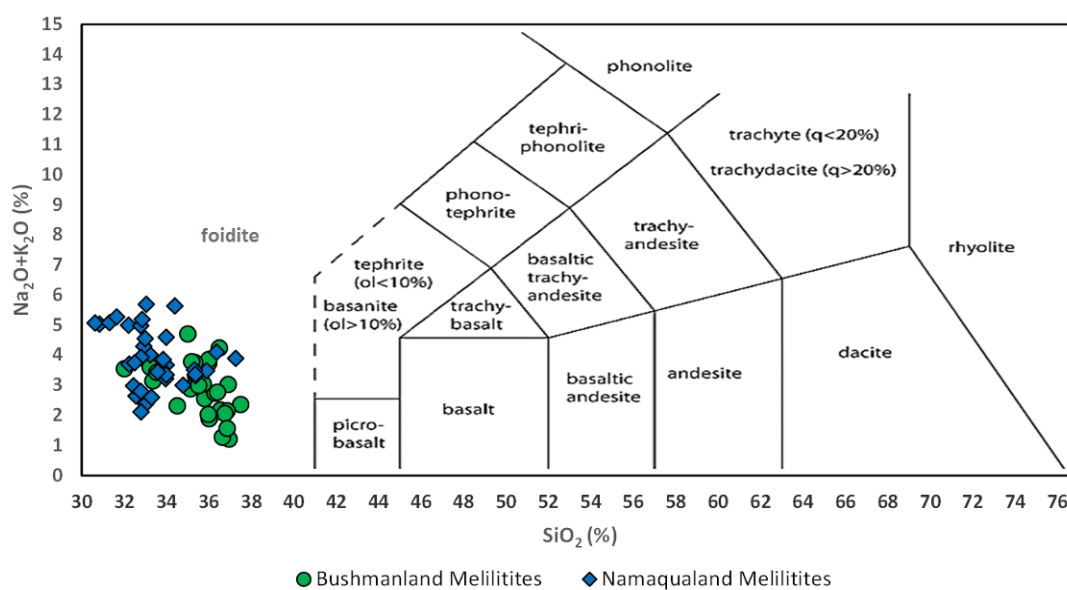


**Figure 34. Total alkalis vs. silica diagram after Le Maitre *et al.* (1989) for the Namaqualand and Bushmanland olivine melilitite samples using normalised, volatile-free data for the non-vesicular melilitites.**

The rocks can be further classified according to the diagram of Le Bas (1989), based on their whole rock  $\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$  versus  $\text{SiO}_2 + \text{Al}_2\text{O}_3$  contents, which is used to distinguish between melilitite, nephelinite and basanite. The results (showing normalized volatile-free data) are shown in Figure 35, which indicates that all of the Namaqualand samples plots within the melilitite field as do the Bushmanland melilitites. The Namaqualand and Bushmanland melilitite samples have similar  $\text{SiO}_2 + \text{Al}_2\text{O}_3$  values, but the Namaqualand samples extend toward higher  $\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}$  (15-22 wt.% for Namaqualand versus 12-19 wt.% for Bushmanland).

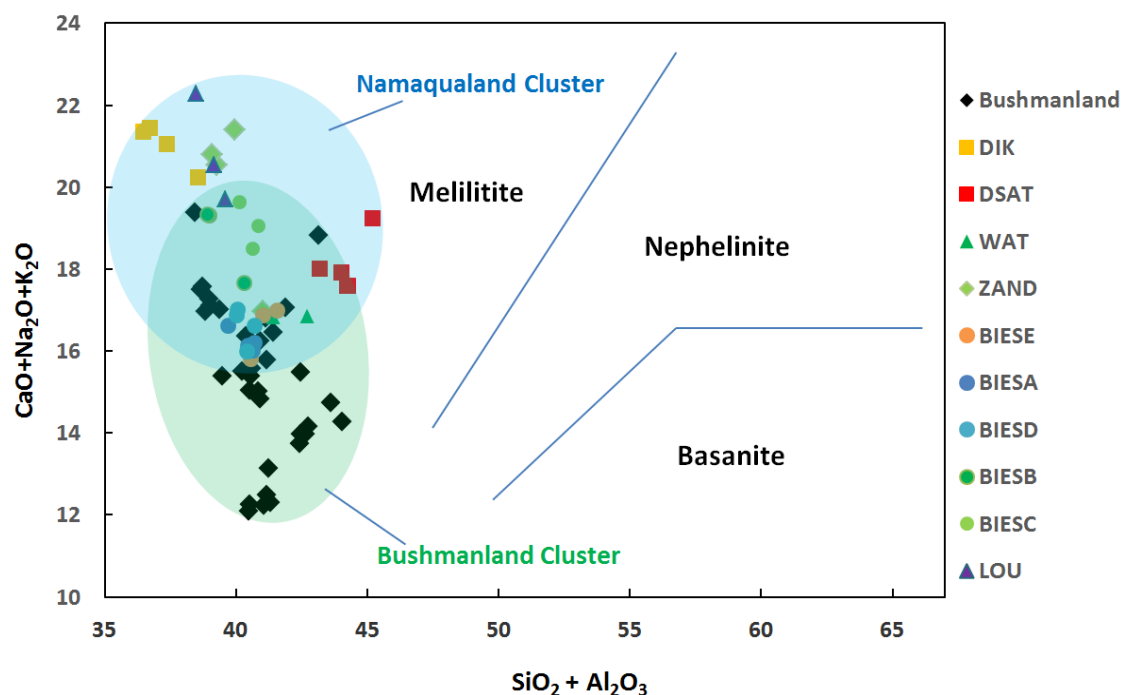


**Figure 35. Melilitite/nephelinite/basanite classification diagram (after Le Bas, (1989) using normalised, volatile free data for the non-vesicular melilitites from Namaqualand and included for comparison data from Bushmanland.**

### 5.2.2 Normative mineralogy criteria.

Normative mineralogies were calculated for the olivine melilitites from their major element compositions using an MS Excel-based calculation worksheet (Naslund, 2017).

Summaries of the normative mineralogies of the samples are provided in Table 9 and Figure 36. All samples are nepheline-, leucite- and larnite-normative, indicating their alkaline and potassic compositions and extreme silica undersaturation. Excluding the vesicular melilitites, samples from the BIESA, BIESD and BIESE pipes are relatively uniform in their normative mineralogy (both within and between pipes), as are samples from the BIESB and BIESC melilitite pipes. Samples from the DIK pipe are highly variable in terms of normative diopside content, and the vesicular DIK melilitites have much higher normative diopside than the non-vesicular samples. There are also significant differences between samples within the DSAT and LOU pipes, mainly in terms of normative olivine and diopside content.

The normative results were used to classify the samples as nephelinites versus melilitites on the basis of normative larnite vs normative nepheline content, after Woolley *et al.* (1996; Figure 37). They selected a threshold between the two rock types at 10% normative larnite, with melilitites having higher values than this. Of the melilitite samples in this study, only those from BIESC BIESD, DIK and one from BIESA fall at greater than 10% normative larnite. With the exception of some samples from DIK, samples from these localities qualify as olivine melilitites on the basis of petrography, by having greater than 10% modal melilite. However, samples from other localities with >10% modal

melilite (e.g., WAT) are classified as nephelinites on the basis of this normative mineralogical criterion.

**Table 9. Normative mineralogy for the Namaqualand olivine melilitite samples.**

| Pipe Name:            | Dikdoorn         |         |               |                  |                  |         |                  |                  | Dikdoorn Satellite |         |              |         |        |
|-----------------------|------------------|---------|---------------|------------------|------------------|---------|------------------|------------------|--------------------|---------|--------------|---------|--------|
| CIPW Norm Mineral ID: | DIK-10           | DIK-11  | DIK-12        | DIK-13           | DIK-VM1          | DIK-VM2 | DIK-VM3          | DIK-VM4          | DSAT-1             | DSAT-2  | DSAT-3A      | DSAT-3B | DSAT-4 |
| Olivine               | 33.5             | 28.9    | 32.4          | 32.3             | 26.2             | 26.2    | 27.3             | 24.1             | 11.2               | 15.8    | 16.5         | 15.9    | 19.9   |
| diopside              | 0.0              | 10.3    | 0.0           | 0.0              | 23.7             | 25.1    | 25.7             | 21.5             | 34.1               | 31.6    | 30.3         | 31.2    | 27.0   |
| ilmenite              | 12.6             | 13.7    | 12.6          | 13.1             | 11.8             | 11.8    | 12.2             | 11.7             | 13.6               | 13.9    | 13.7         | 13.9    | 13.0   |
| Larnite               | 20.9             | 16.2    | 20.8          | 20.5             | 2.9              | 2.3     | 2.6              | 10.4             | 4.7                | 3.7     | 4.7          | 3.9     | 6.3    |
| Leucite               | 11.5             | 11.1    | 9.7           | 16.6             | 7.5              | 5.0     | 5.6              | 9.6              | 5.9                | 5.7     | 6.4          | 5.9     | 5.3    |
| plagioclase           | 0.0              | 4.3     | 0.0           | 0.0              | 15.0             | 13.4    | 12.7             | 10.4             | 11.9               | 11.3    | 10.3         | 11.4    | 11.4   |
| nepheline             | 6.0              | 6.2     | 7.2           | 5.8              | 3.4              | 6.7     | 4.1              | 2.8              | 10.3               | 9.8     | 10.0         | 9.7     | 8.7    |
| Apatite               | 5.8              | 5.3     | 5.8           | 5.5              | 5.8              | 5.9     | 6.1              | 5.7              | 4.1                | 3.8     | 3.9          | 3.7     | 4.2    |
| magnetite             | 2.7              | 3.8     | 1.9           | 3.2              | 3.6              | 3.6     | 3.6              | 3.5              | 3.7                | 4.0     | 3.9          | 4.0     | 3.9    |
| Other                 | 7.0              | 0.2     | 9.8           | 3.0              | 0.1              | 0.1     | 0.1              | 0.2              | 0.5                | 0.4     | 0.4          | 0.4     | 0.5    |
| Total                 | 100              | 100     | 100           | 100              | 100              | 100     | 100              | 100              | 100                | 100     | 100          | 100     | 100    |
| Pipe Name:            | Watervaal        |         | Zandkopsdrift | Biesiesfontein E |                  |         | Biesiesfontein A |                  |                    |         |              |         |        |
| CIPW Norm Mineral ID: | WAT-1            | WAT-2   | ZAND-7        | BIESE-1          | BIESE-2          | BIESE-3 | BIES-10          | BIES-11          | BIESA-1            | BIESA-2 | BIESA-VM1    |         |        |
| olivine               | 32.0             | 36.5    | 24.8          | 20.3             | 24.8             | 21.9    | 28.5             | 28.8             | 31.5               | 29.7    | 13.3         |         |        |
| diopside              | 23.6             | 17.5    | 9.8           | 26.1             | 21.5             | 23.5    | 19.1             | 17.8             | 11.6               | 16.5    | 38.3         |         |        |
| ilmenite              | 8.2              | 8.2     | 13.1          | 15.8             | 15.5             | 15.0    | 14.4             | 14.4             | 14.6               | 14.4    | 15.1         |         |        |
| larnite               | 7.4              | 10.0    | 15.1          | 5.4              | 6.3              | 6.3     | 7.6              | 8.1              | 10.9               | 8.5     | 0.2          |         |        |
| leucite               | 8.2              | 8.8     | 12.0          | 5.2              | 5.1              | 7.2     | 10.4             | 11.8             | 14.8               | 11.8    | 11.6         |         |        |
| plagioclase           | 2.9              | 1.0     | 0.0           | 11.4             | 13.6             | 8.8     | 7.4              | 5.8              | 4.6                | 6.4     | 11.4         |         |        |
| nepheline             | 9.9              | 10.3    | 9.0           | 6.9              | 4.7              | 8.9     | 4.6              | 5.4              | 4.0                | 4.7     | 2.2          |         |        |
| apatite               | 4.1              | 4.2     | 4.3           | 4.3              | 3.4              | 4.0     | 3.6              | 3.5              | 3.6                | 3.6     | 4.0          |         |        |
| magnetite             | 3.1              | 3.1     | 3.1           | 4.3              | 4.6              | 4.3     | 4.1              | 4.0              | 4.1                | 4.1     | 3.9          |         |        |
| other                 | 0.4              | 0.4     | 9             | 0.3              | 0.5              | 0.2     | 0.3              | 0.3              | 0.3                | 0.3     | 0.0          |         |        |
| Total                 | 100              | 100     | 100.0         | 100              | 100              | 100     | 100              | 100              | 100                | 100.0   | 100.0        |         |        |
| Pipe Name:            | Biesiesfontein D |         |               |                  | Biesiesfontein B |         |                  | Biesiesfontein C |                    |         | Louisfontein |         |        |
| CIPW Norm Mineral ID: | BIESD-1          | BIESD-2 | BIESD-3       | BIESD-4          | BIESB-1          | BIESB-2 | BIESB-3          | BIESC-1          | BIESC-2            | BIESC-3 | LOU-2        | LOU-3   | LOU-4  |
| olivine               | 25.0             | 25.4    | 21.1          | 24.9             | 36.9             | 32.8    | 36.0             | 34.2             | 33.5               | 34.6    | 29.5         | 31.5    | 33.2   |
| diopside              | 19.9             | 19.0    | 25.2          | 22.1             | 3.7              | 14.3    | 5.1              | 10.7             | 7.8                | 11.9    | 8.9          | 0.0     | 4.0    |
| ilmenite              | 15.1             | 15.1    | 15.7          | 15.2             | 11.3             | 11.8    | 11.4             | 9.9              | 10.6               | 10.0    | 13.3         | 12.2    | 9.8    |
| larnite               | 8.5              | 8.5     | 5.9           | 5.8              | 17.3             | 11.0    | 16.7             | 14.6             | 16.1               | 13.6    | 16.2         | 22.6    | 18.8   |
| leucite               | 5.3              | 5.8     | 4.4           | 4.9              | 14.4             | 10.0    | 12.8             | 9.2              | 9.2                | 7.3     | 10.8         | 13.9    | 15.2   |
| plagioclase           | 10.6             | 9.3     | 12.0          | 10.1             | 2.0              | 5.6     | 3.2              | 1.1              | 2.2                | 3.7     | 6.2          | 0.0     | 1.3    |
| nepheline             | 7.0              | 8.1     | 6.7           | 8.2              | 5.7              | 5.6     | 5.6              | 12.2             | 12.0               | 10.7    | 6.7          | 10.0    | 10.6   |
| apatite               | 3.9              | 3.9     | 3.8           | 4.1              | 5.1              | 5.0     | 5.3              | 4.3              | 4.7                | 4.4     | 4.2          | 4.8     | 3.6    |
| magnetite             | 4.4              | 4.4     | 4.4           | 4.5              | 3.5              | 3.6     | 3.5              | 3.7              | 3.7                | 3.7     | 3.8          | 3.3     | 2.8    |
| other                 | 0.4              | 0.4     | 0.8           | 0.3              | 0.2              | 0.3     | 0.3              | 0.1              | 0.2                | 0.1     | 0.4          | 1.7     | 0.8    |
| Total                 | 100              | 100     | 100           | 100              | 100              | 100     | 100              | 100              | 100                | 100     | 100          | 100     | 100    |

*\*Other includes the minerals pyrite, acmite, kaliophilite, corundum which occur in low amounts.*

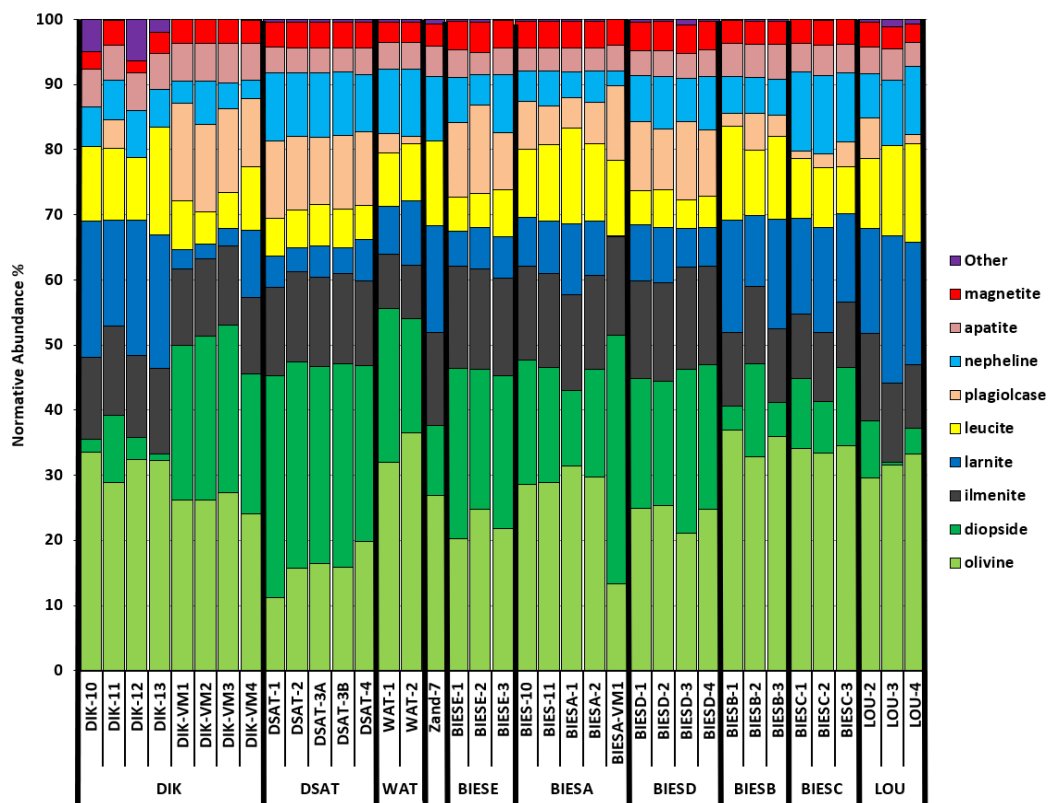


Figure 36. Summarized normative mineralogy for the olivine melilitite samples arranged from North to South.

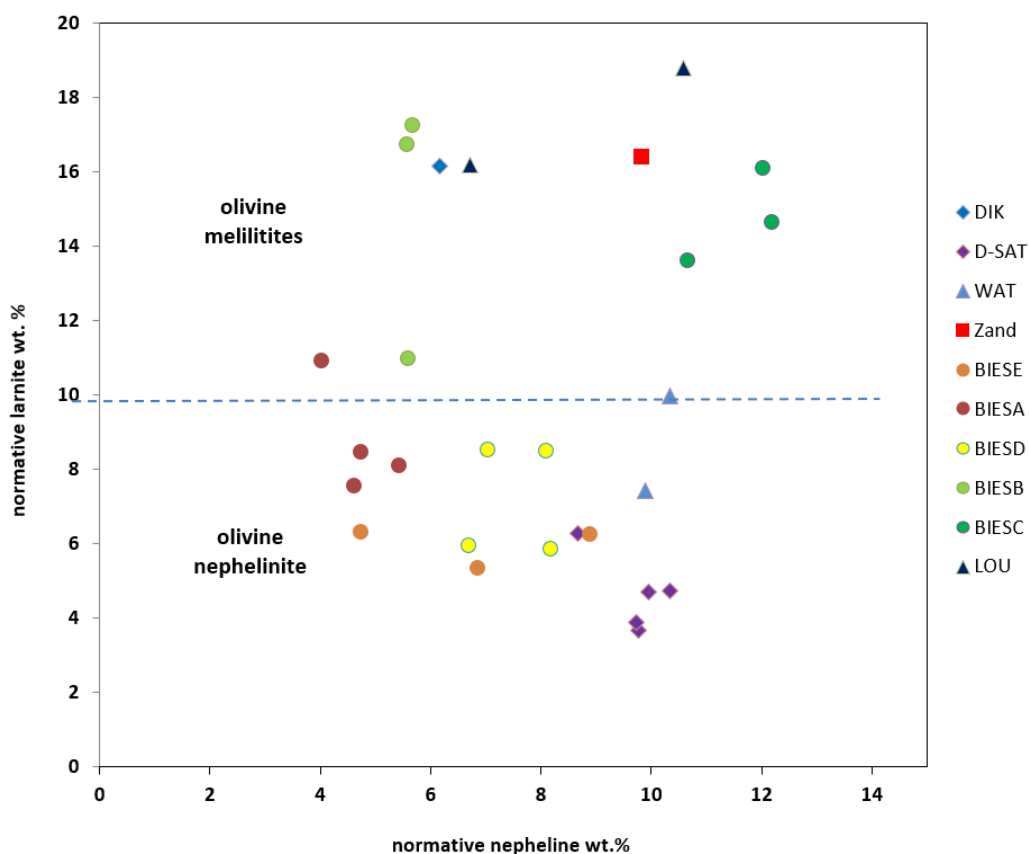


Figure 37. Normative classification of melilitite samples according to Woolley *et al.* (1996). Only the non-vesicular melilitites are plotted.

The various classification systems for the Namaqualand melilitites are compared (Table 10). There are some differences between the modal classification of Le Bas and Streckeisen (1991) and the normative mineralogical classification of Woolley *et al.* (1996), however, 23 out of 43 samples have the same rock classification. The geochemical classification method used by Le Bas (1989) simply classifies all the samples as melilitites while the alkalis vs silica geochemical classification method Le Maitre *et al.* (1989) classifies all the rocks as foidites. When comparing the Mg # of the pipes with the rock classifications no trend could be identified suggesting the rock classifications show no correlation to the Mg # of the pipes.

**Table 10: A Comparison of methods used to classify the Namaqualand melilitite samples.**

| Pipe  | Sample Name     | Modal classification<br>(Le Bas and<br>Streckeisen, 1991) | Normative<br>classification<br>(Woolley <i>et al.</i> , 1996) | Geochemical<br>classification<br>(Le Bas, 1989) | Geochemical<br>classification<br>Le Maitre <i>et al.</i><br>(1989) | MG # |
|-------|-----------------|-----------------------------------------------------------|---------------------------------------------------------------|-------------------------------------------------|--------------------------------------------------------------------|------|
| DIK   | DIK-10 A, B     | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 58   |
|       | DIK-11 A, B     | olivine nephelinite                                       | olivine melilitite                                            | melilitite                                      | foidite                                                            | 60   |
|       | DIK-12 A, B     | olivine nephelinite                                       | olivine melilitite                                            | melilitite                                      | foidite                                                            | 52   |
|       | DIK-13          | olivine nephelinite                                       | olivine melilitite                                            | melilitite                                      | foidite                                                            | 48   |
|       | DIK-VM1         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 49   |
|       | DIK-VM2         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 48   |
|       | DIK-VM3         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 51   |
|       | DIK-VM4         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 57   |
| DSAT  | DSAT-1          | nephelinite                                               | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 59   |
|       | DSAT-2          | nephelinite                                               | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 58   |
|       | DSAT-3A, B      | nephelinite                                               | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 71   |
|       | DSAT-4          | nephelinite                                               | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 51   |
| WAT   | WAT-1           | olivine melilitite                                        | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 70   |
|       | WAT-2           | olivine melilitite                                        | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 71   |
| ZAND  | ZAND-7          | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 58   |
| BIESE | BIESE-1         | nephelinite                                               | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 49   |
|       | BIESE-2         | nephelinite                                               | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 60   |
|       | BIESE-3         | nephelinite                                               | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 60   |
| BIESA | BIES-10 A, B, C | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 58   |
|       | BIES-11 A, B    | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 58   |
|       | BIESA-1         | olivine nephelinite                                       | olivine melilitite                                            | melilitite                                      | foidite                                                            | 58   |
|       | BIESA-2         | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 58   |
|       | BIESA-VM1       | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 65   |
| BIESD | BIESD-1         | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 49   |
|       | BIESD-2         | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 50   |
|       | BIESD-3         | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 49   |
|       | BIESD-4         | olivine nephelinite                                       | olivine nephelinite                                           | melilitite                                      | foidite                                                            | 50   |
|       | BIESB-1         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 64   |
| BIESB | BIESB-2         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 62   |
|       | BIESB-3         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 60   |
| BIESC | BIESC-1         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 62   |
|       | BIESC-2         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 50   |
|       | BIESC-3         | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 50   |
| LOU   | LOU-2           | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 57   |
|       | LOU-3           | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 59   |
|       | LOU-4           | olivine melilitite                                        | olivine melilitite                                            | melilitite                                      | foidite                                                            | 58   |

## 5.3. Elemental co-variations.

### 5.3.1 Major Oxides.

The major element data for the Namaqualand melilitites pipes is presented as oxides vs. wt.% MgO in Figure 38. The Namaqualand melilitites display significant variations in MgO, from ~7 to ~17 wt.%. Each pipe is relatively homogenous and samples from the same pipes cluster closely together for most elements. MgO displays a weak positive correlation with SiO<sub>2</sub> and strong negative

correlations with  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{FeO}_{\text{tot}}$ . Correlations of  $\text{MgO}$  with  $\text{CaO}$ ,  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$  and  $\text{P}_2\text{O}_5$  are very weak to non-existent. Olivine control lines are shown to indicate the expected compositional variation due to olivine fractionation or accumulation.

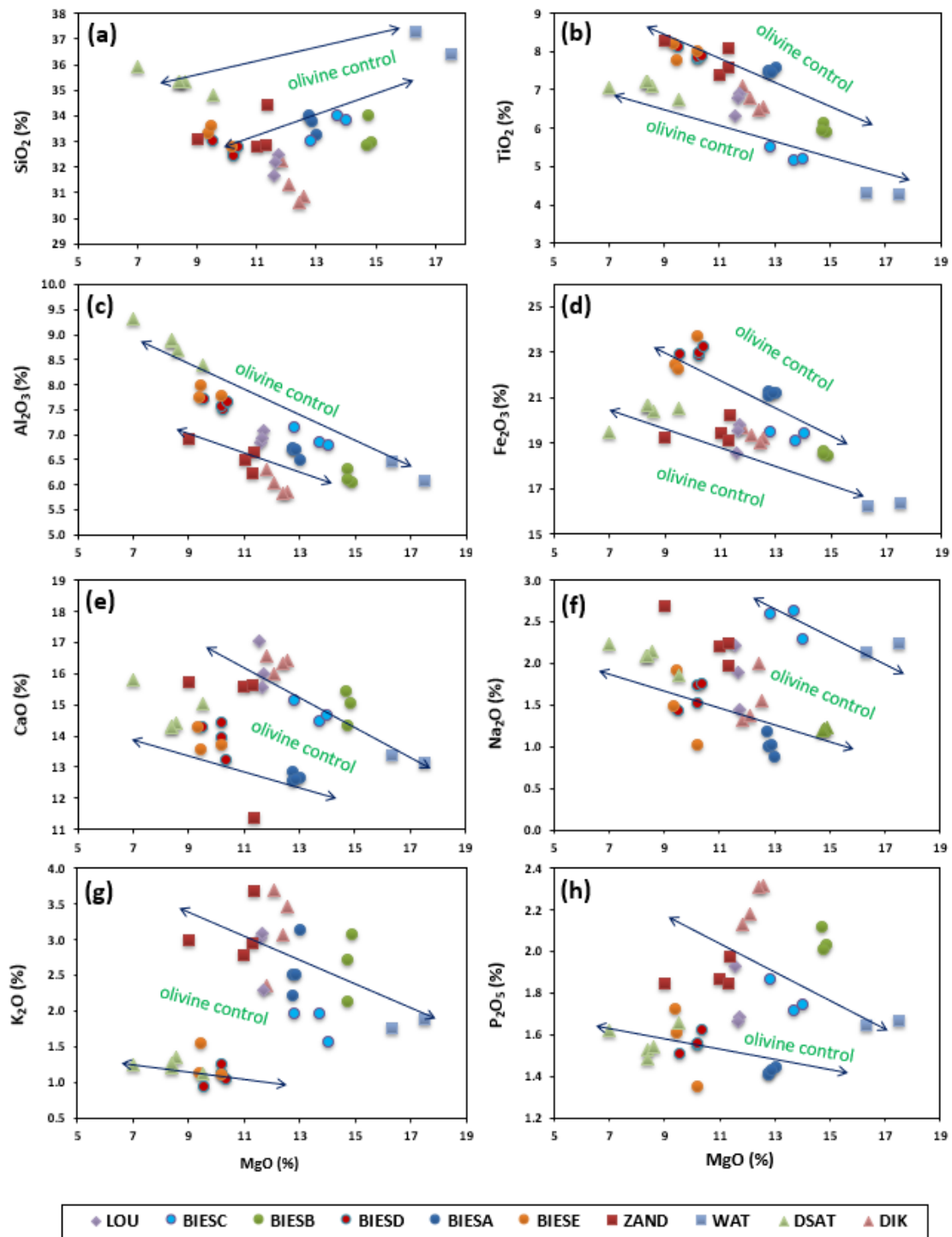


**Figure 38.** Plots of  $\text{MgO}$  versus other major oxides normalized volatile free for the Namaqualand olivine melilitite samples excluding the vesicular melilitites. The panels show the following major oxides plotted against  $\text{MgO}$  (a)  $\text{SiO}_2$ , (b)  $\text{TiO}_2$ , (c)  $\text{Al}_2\text{O}_3$ , (d)  $\text{Fe}_2\text{O}_3$ , (e)  $\text{CaO}$ , (f)  $\text{Na}_2\text{O}$ , (g)  $\text{K}_2\text{O}$  and (h)  $\text{P}_2\text{O}_5$ . The ZAND data is from Ogungbuyi (2019) and Moore (1979).

### 5.3.2 Major element comparison.

By major element composition, Namaqualand olivine melilitites are broadly similar to a variety of other ultramafic, silica-undersaturated igneous rocks, including southern African Group 1 and Group 2 kimberlites, and olivine melilitites from the neighbouring Bushmanland cluster, as well as those from the Rhine Graben (Germany) and Ocean Island (OI) olivine melilitites from Hawaii.

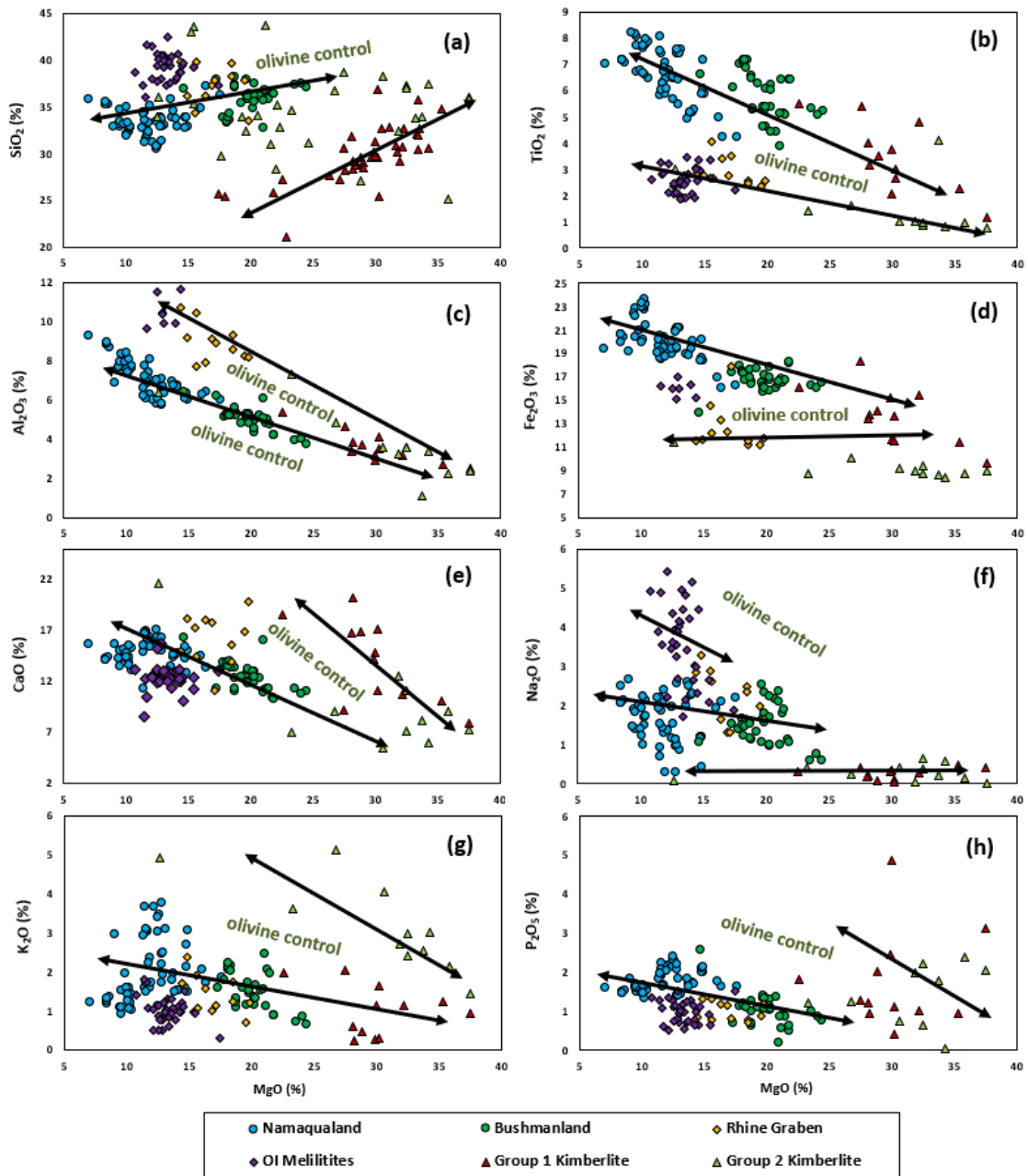


**Figure 39.** Major element comparison with comparable igneous rocks. Plots display wt.% MgO versus: a). SiO<sub>2</sub>, (b) TiO<sub>2</sub>, (c) Al<sub>2</sub>O<sub>3</sub>, (d) Fe<sub>2</sub>O<sub>3</sub>, (e) CaO, (f) Na<sub>2</sub>O, (g) K<sub>2</sub>O, (h) P<sub>2</sub>O<sub>5</sub>. In each plot the Namaqualand and Bushmanland olivine melilitites are compared to the Rhine Graben melilitites (Wilson, 1995), a suite of ocean island melilitites (Maaloe *et al.*, 1992), as well as Group 1 and Group 2 kimberlites (Becker & le Roex, 2006; Le Roex *et al.* 2003; Coe *et al.* 2008). The Bushmanland data used was from (Moore, 1979).

The Namaqualand and Bushmanland data form distinct linear trends (Figure 39)) for all of the oxides plotted against MgO, which in most cases is fairly well explained by the removal or addition of olivine. The Group 1 and Group 2 kimberlite samples all plot away from the melilitite data as they have a much higher MgO content (~25 to 38%); however, in many cases the Group 1 kimberlite data appear to form an extension of the same trend as the Namaqualand and Bushmanland data. The Rhine Graben and Hawaiian melilitites form distinct clusters on most graphs and have higher SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and Na<sub>2</sub>O, MgO and Ni and negative correlations between MgO and incompatible elements, such as Zr (Figure 40). The melilitite pipes that have yielded the most primitive, MgO-rich melilitite samples, such as WAT, therefore, have the highest content of Ni and Cr and the lowest incompatible element contents, while samples from the pipes yielding the most MgO-poor melilitites, such as DSAT have the lowest and highest compatible and incompatible element abundances, respectively.

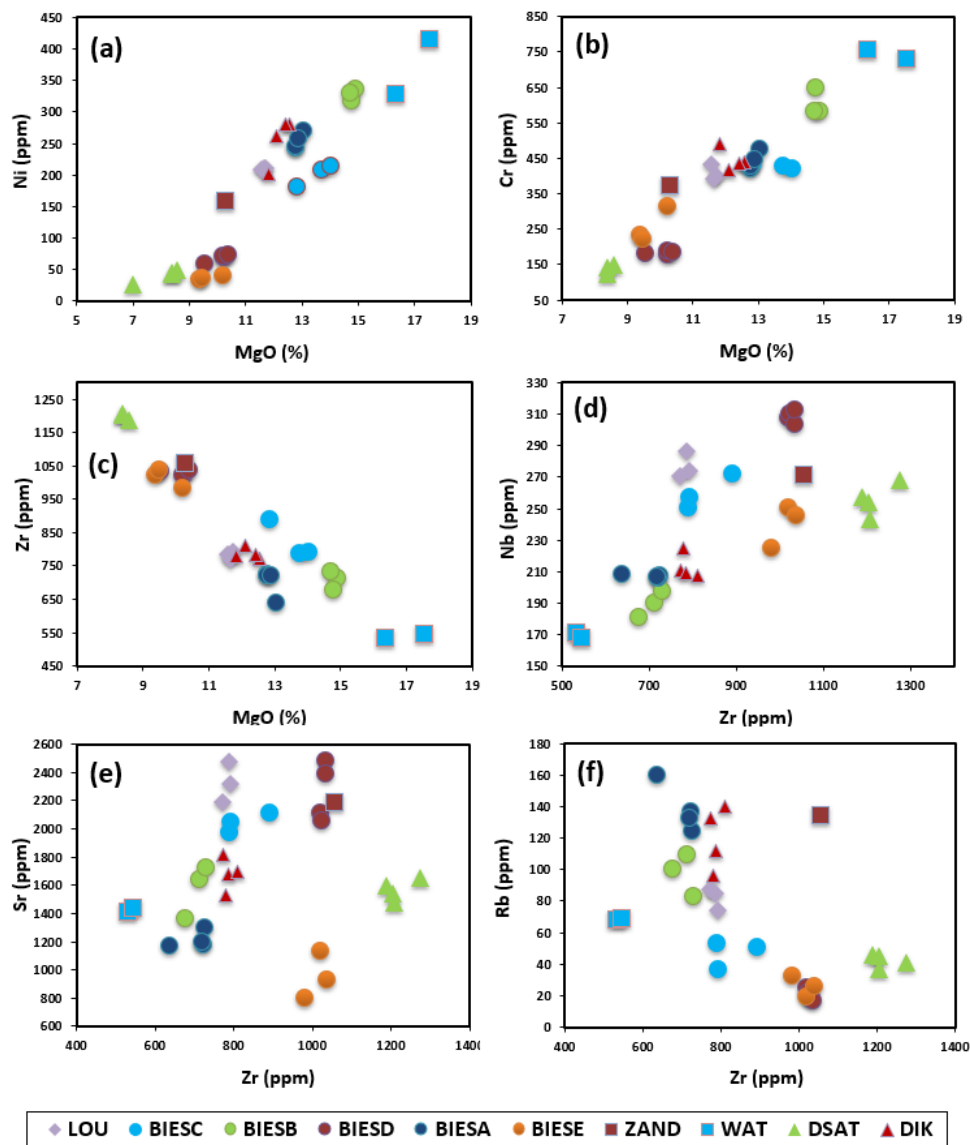


**Figure 40.** Plots displaying compatible and incompatible element variations of the Namaqualand melilitites (normalised volatile-free and excluding the vesicular melilitites) (a), Ni vs. MgO. (b), shows Cr vs. MgO. (c), Zr vs. MgO. (d), Nb vs. Zr. (e), Sr vs. Zr and (f), and Rb vs. Zr.

The plots of Zr versus Nb, Sr and Rb show a moderate correlation for Nb and a non-correlation for Sr and Rb. This set of poor correlations could indicate that incompatible element variations are not entirely controlled by fractional crystallization processes.

### 5.3.3 REE patterns of the olivine melilitites.

The average chondrite-normalised rare earth element (REE) patterns for the different Namaqualand pipe localities (Figure 41) show a steep gradient from the LREE to the HREE with La ranging from 324 to 1008 and Lu from 7 to 11 times chondrite abundances. Samples from individual pipes have nearly identical rare earth element patterns and for this reason, only the average melilitite composition of each pipe is plotted. Overall, there are only moderate differences between the pipe averages in terms of LREE enrichment and HREE depletion (i.e.,  $(\text{La}/\text{Sm})_N = 2.7$  to 6.7 and  $(\text{La}/\text{Yb})_N = 30$  to 79). The most LREE enriched pipe is BIES-C (mean  $(\text{La}/\text{Sm})_N = 6.6$ ), followed by LOU (mean  $(\text{La}/\text{Sm})_N = 5.1$ ) and while the least LREE enriched pipes are BIES-B (mean  $(\text{La}/\text{Sm})_N = 2.8$ ) and BIES-A (mean  $(\text{La}/\text{Sm})_N = 3.0$ ).

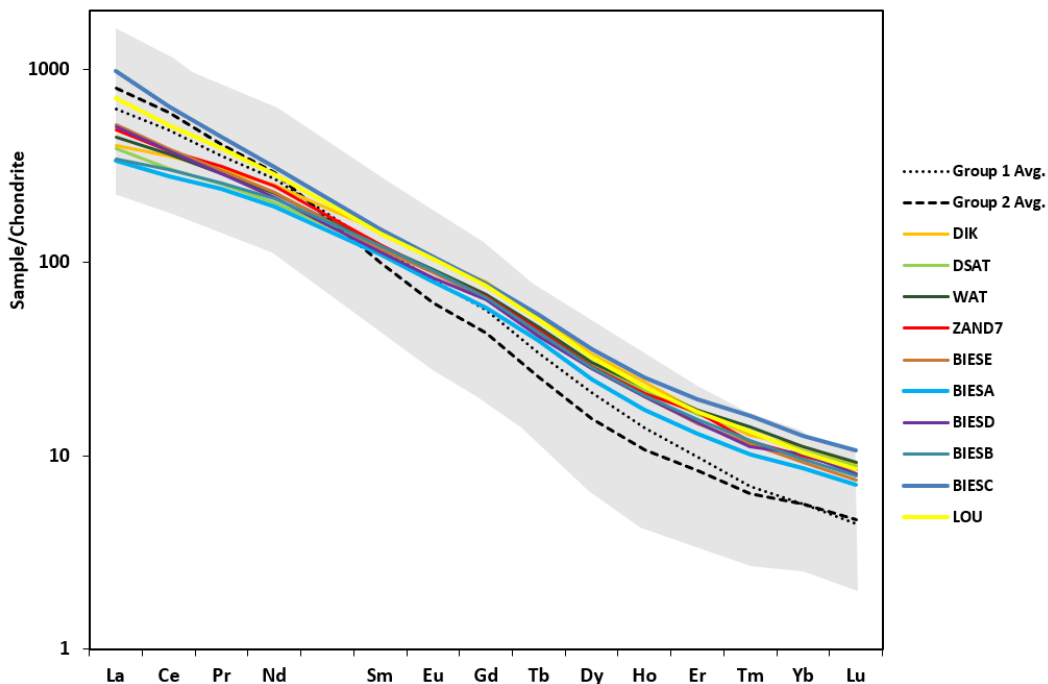


**Figure 41.** The mean C1 chondrite-normalized REE patterns for samples from the nine Namaqualand melilitite pipes compared to dashed lines representing the average Group 1 and Group 2 kimberlites from Becker & le Roex (2006). The grey field represents the combined field for Group 1 and Group 2 kimberlites (same data source). The data shown exclude those for the vesicular melilitites. Normalizing values for C1 chondrite are from Evensen *et al.* (1978).

The Namaqualand data compare very closely with the data for Group 1 and Group 2 kimberlites, which in general have a higher concentration of HREE and lower LREE. The Group 2 kimberlites specifically have the highest content of HREE and lowest content of LREE. The results shown in Figure 42 compare the average of the Namaqualand melilitite pipes with that of the Bushmanland melilitite pipes as well as the Group 1 and Group 2 kimberlite pipes in South Africa showing that the

kimberlite pipes are generally much more depleted in HREE and more enriched in LREE when compared with the Namaqualand and Bushmanland melilitites. The kimberlites, however, have values that are closer to the range of HREEs for the Bushmanland melilitites, however, the average of the kimberlite pipes is much lower for LREE than the range in values for both the Namaqualand and Bushmanland melilitites.

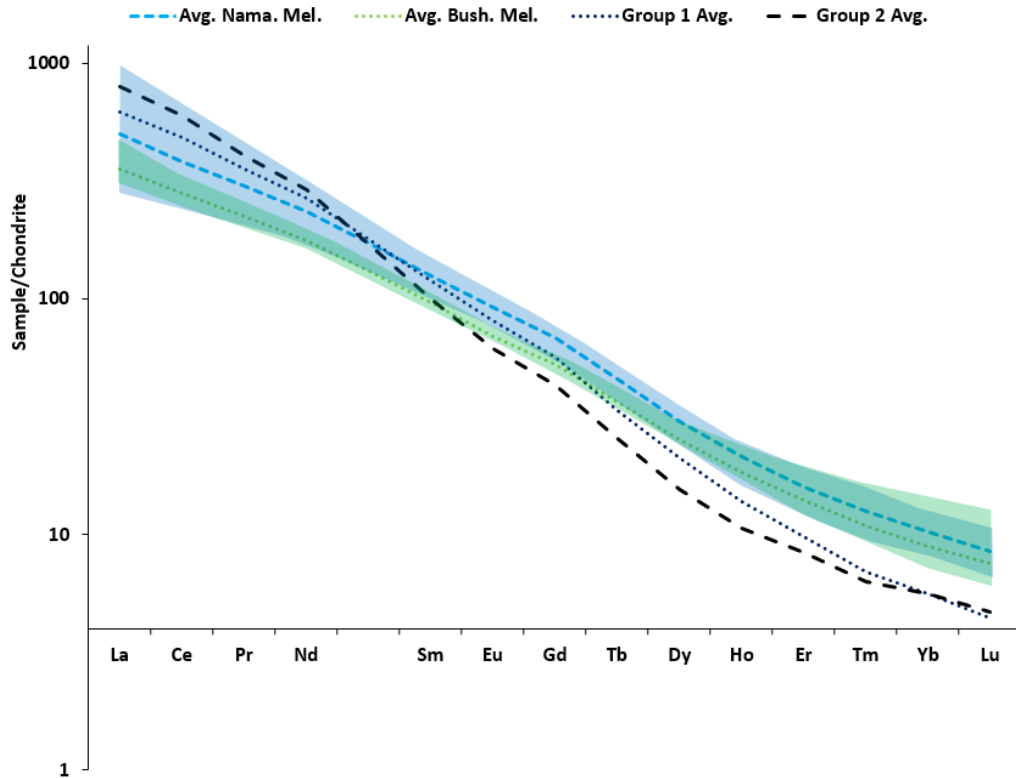


**Figure 42: The mean C1 chondrite-normalized REE patterns for the average of the Namaqualand and Bushman melilitite pipes compared to dashed lines representing the average Group 1 and Group 2 kimberlites from Becker & le Roex (2006) and Le Roux (2003). The green field represents the combined field for the Namaqualand melilitite pipes while the blue field represents the combined field for the Bushmanland melilitite pipes. The data shown exclude those for the vesicular melilitites. Normalizing values for C1 chondrite are from Evensen *et al.* (1978).**

#### 5.3.4 Trace element results.

The trace element compositions of the Namaqualand melilitites form a co-linear relationship when compared with the Bushmanland melilitites (Figure 43). The trace element compositions from these two clusters are further compared to those of the Group 1 and Group 2 kimberlites, OI, melilitites and Rhine Graben melilitites. The data when compared forms a generally positive correlation for compatible elements such as Ni and Cr plotted against MgO while incompatible elements such as Zr against MgO show a negative correlation between the Namaqualand and Bushmanland melilitites.

A plot of Nb against Zr shows a positive correlation for the Namaqualand melilitites to the Bushmanland melilitites which can be extended between the Group 2 and Group 1 kimberlites which

have some of the highest Zr and Nb values. The O.I. melilitites have the greatest depletion in Nb and Zr.

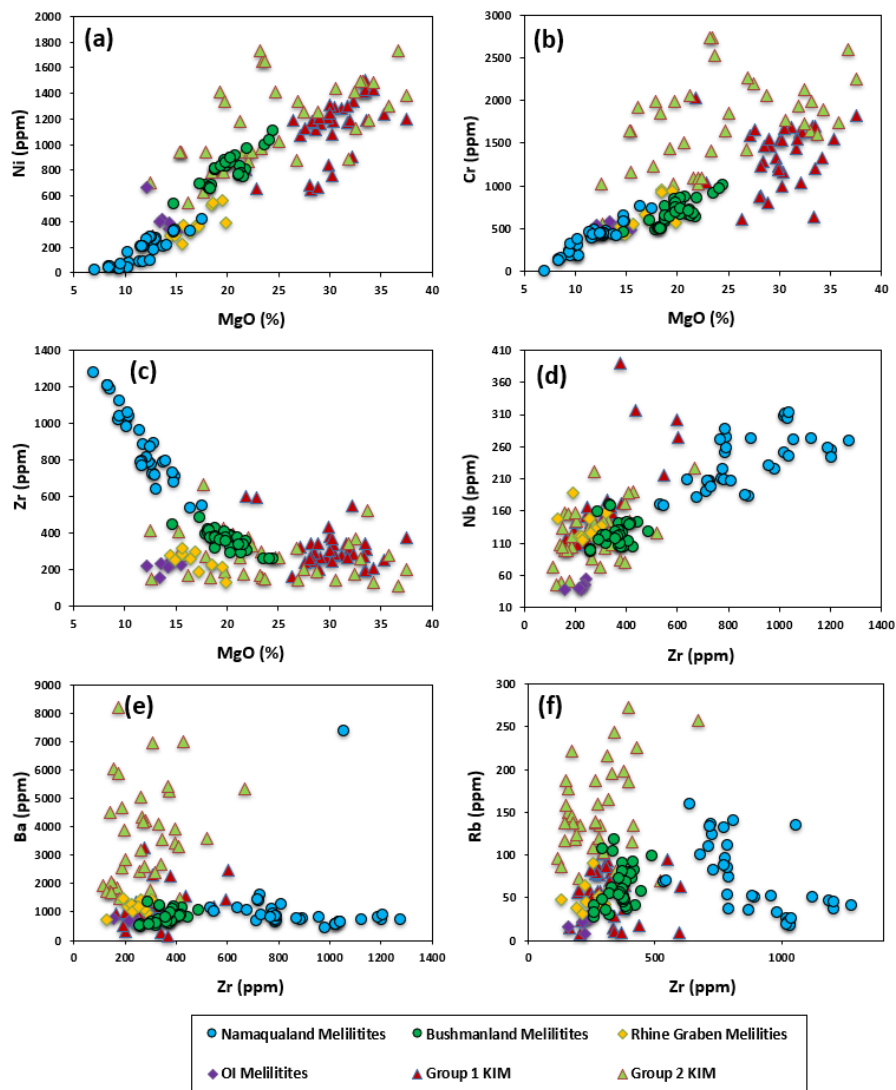


**Figure 43: Plots displaying trace element data for the Namaqualand melilitites along with comparable igneous rocks. Panels show: (a) Ni vs. MgO, (b) Cr vs. MgO, (c) MgO vs. Zr, (d) Zr vs. Nb, (e) Zr vs. Ba, and (f) Zr vs. Rb. The Namaqualand and Bushmanland olivine melilitites data are compared to the data for the Rhine Graben melilitites (Wilson, 1995), a suite of ocean island melilitites (Maaloe *et al.*, 1992), as well as Group 1 and Group 2 Kimberlites (Becker & le Roex, 2006, Coe *et al.*, 2008 and Le Roex *et al.*, 2003). The LKF-1 and GNF-2 pipes from the Becker and Le Roex (2006) study were removed from this presentation as the results are anomalous and don't seem to represent fresh kimberlite magma.**

The plot of Ba against Zr shows a trend with decreasing Zr between the Namaqualand and Bushmanland melilitites while Ba remains relatively constant. The plot of Rb against Zr shows a negative correlation with a decrease in both elements during the transition from the Namaqualand to the Bushmanland melilitites. The group 1 kimberlites, the O.I. melilitites and the Rhine Graben melilitites are generally depleted in Rb and Zr.

Two anomalous kimberlite samples from the Group 1 kimberlite data set of Becker and Le Roex (2006) were removed as they both represent very unusual compositions in that they have higher MgO,

Zr and Nb compositions than all the other samples. The reason for this is unclear, however, they appear to be off-craton kimberlites and are unlikely to represent fresh magmatic compositions.

## 5.4. Normalized REE and incompatible element patterns:

### 5.4.1 REE patterns of the country rock samples compared with an average of Namaqualand Melilitites.

The REE patterns for the country rocks samples are compared with the pattern for the average Namaqualand melilitite (Figure 40). The country rock samples generally have REE patterns with shallower slopes and relatively flat MREE-HREE patterns, and all have significant negative Eu anomalies. This Eu anomaly is commonly associated with the fractional crystallization of plagioclase (Weill and Drake, 1973). Additionally, most country rock samples have variable negative and positive Ce anomalies, which are likely due to low-temperature alteration under oxidising conditions (e.g., Henderson, 1984). The melilitites in contrast have steeper REE patterns overall, with stronger LREE enrichment and the slope is relatively constant with no anomalies.

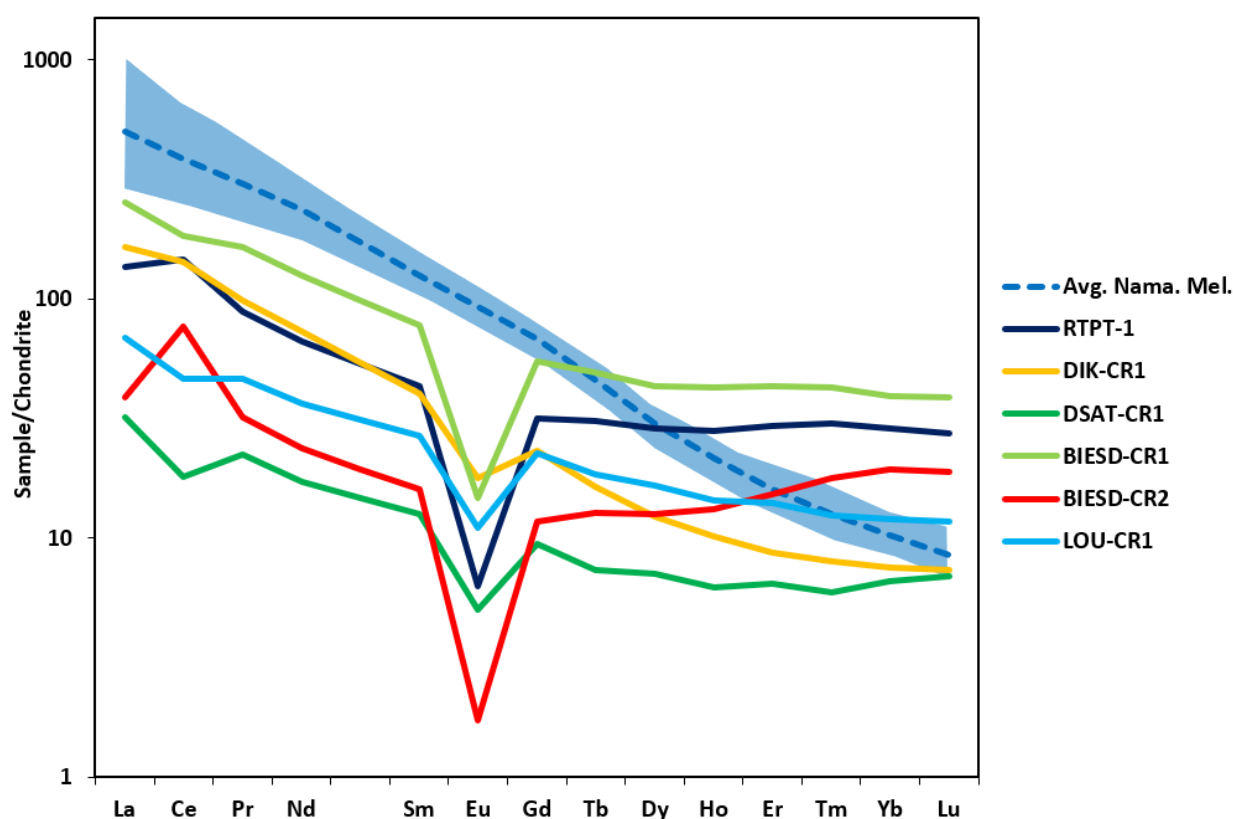


Figure 44. Chondrite-normalized REE patterns for country rock samples compared with that for the average Namaqualand melilitite. The samples have all been normalized using the values for C1 chondrites from Evensen *et al.* (1978). The dashed line represents the average value for the Namaqualand melilitites while the blue-shaded area shows the range of values for the same pipes.

### 5.4.2 *Primitive mantle-normalized patterns for olivine melilitites.*

Figure 45 shows average primitive mantle-normalised patterns for the 9 sampled Namaqualand melilitite pipes. The pipes have similar patterns, but there are some variations in the degree of enrichment or depletion in certain elements, in particular, the most highly incompatible elements (Rb, Ba, Nb, Th, U, K and the LREE) as well as Zr and Hf. Samples from all pipes are characterised by low Rb, Ba and Th abundances relative to U and Nd concentrations except for the Zand-7 sample which has a positive Ba. The Namaqualand samples also have distinct negative K and Pb anomalies.

The Namaqualand melilitites all have distinctly low Th when compared to U giving these rocks, particularly low Th/U ratios which are much lower than those of nearly all terrestrial mafic magmas including the Bushmanland melilitites and Group1 and 2 kimberlites (Becker & le Roex, 2006). In addition, Th and U are relatively similar in incompatibility during mantle melting for most minerals, therefore, it is difficult to cause the low Th/U ratios by either melting of common exotic residual minerals or by fractional crystallization processes.

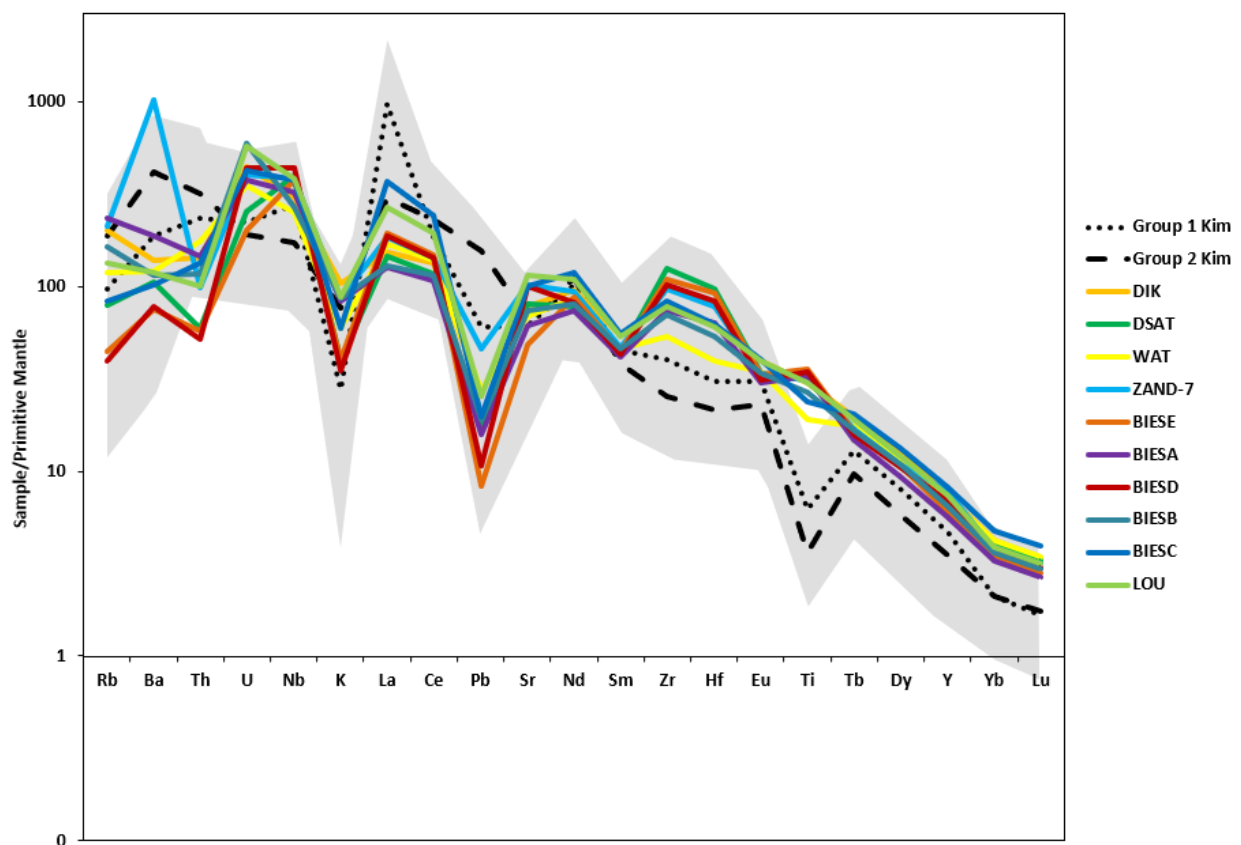


**Figure 45. Average primitive mantle-normalised incompatible element patterns for the nine sampled Namaqualand melilitite pipes. The primitive mantle values from McDonough & Sun (1995) were used for normalisation. The Group 1 and Group 2 kimberlites values are averaged from the values from Becker & le Roex (2006) and Le Roux (2003). The shaded area shows the range of values for Group 1 kimberlites obtained from the same study.**

### 5.4.3 Primitive mantle-normalized patterns for country rocks.

Figure 46 shows the trace element patterns for the country rock samples compared to that for the average of all Namaqualand melilitite samples as well as the range of values for the Namaqualand pipes. There is a clear difference in the patterns between the average of the olivine melilitite samples and all the other country rock samples. Most notably, the country rocks samples all show positive anomalies in K and Pb as well as higher abundances of these elements than the average melilitite. Similarly, the country rock samples show lower abundances of most minerals but particularly of Sr,

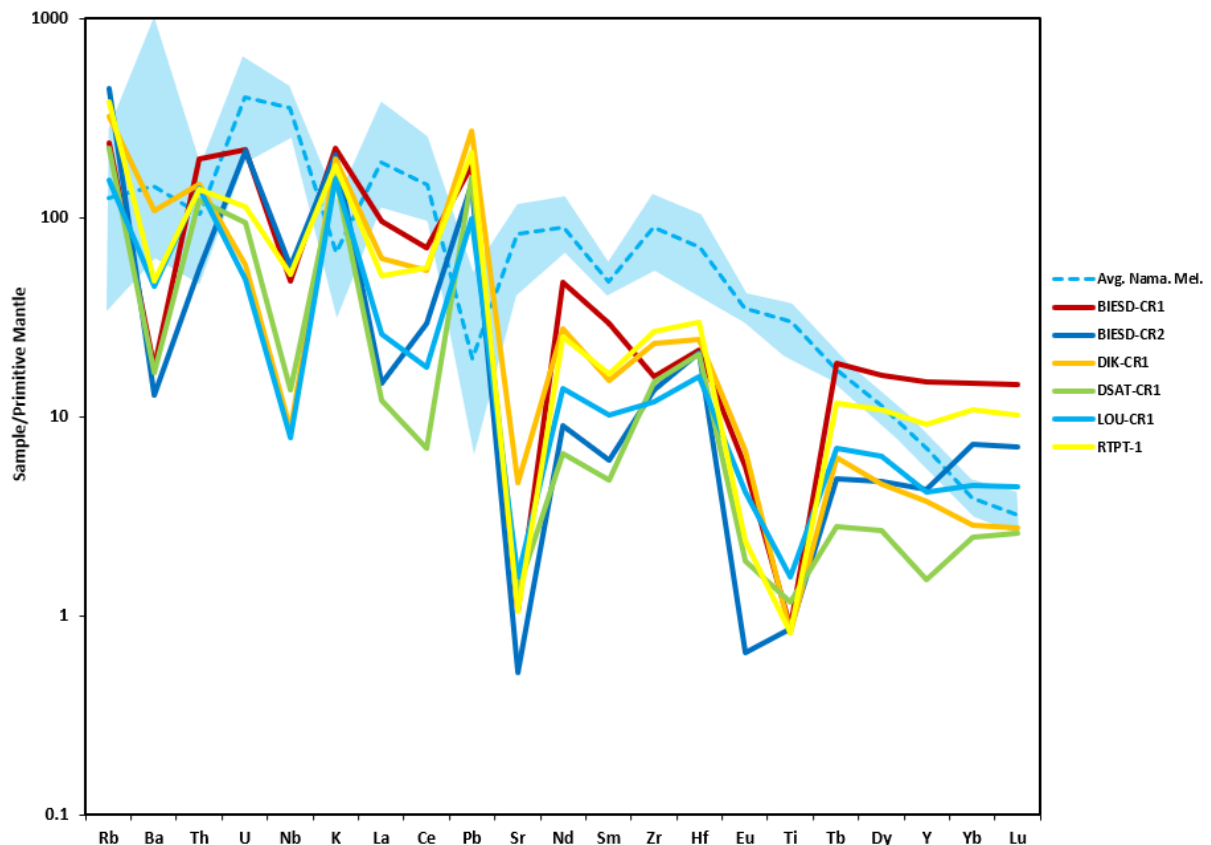


**Figure 46. Primitive mantle-normalised incompatible element patterns for samples of crustal basement adjacent to Namaqualand olivine melilitite pipes, compared with the patterns for the average Namaqualand melilitite (blue dashed line) and the range in values for the Namaqualand melilitites (blue shaded area). The primitive mantle values from McDonough & Sun (1995) were used for the normalization of all the data.**

La, Ce, Ba, Eu, Nb and Ti, with pronounced negative anomalies in Ba, Nb, Sr, Eu and Ti. This causes the country rock samples to have far lower Ba/Rb, Nb/U, Ce/Pb and higher Rb/Sr ratios than the melilitites. The Namaqualand pipes have distinctly low K and Pb compared with the country rock samples and much higher U, Nb, La, Ce, Sr, Nd, Sm, Zr, Hf, Eu, and Ti.

## 5.5. Whole rock Sr, Nd and Pb radiogenic isotope data.

Whole rock Sr, Nd and Pb radiogenic isotope data were obtained for 18 Namaqualand whole rock melilitite samples from nine pipes (Appendix F ). Data were only obtained from non-vesicular

melilitite samples because these were least altered and most likely to provide isotope data representative of the melilitites' mantle sources. Even so,  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios appear to have been somewhat affected by low-temperature exchange. As a result, Sr isotope ratios were obtained on both un-leached sample powders and powders leached with cold 4 M HCl (e.g., Mahoney, 1987). Such leaching is done routinely for the measurement of Sr isotopes in oceanic basalts and it has been found to be also useful for clarifying mixing relationships involving Sr isotopes in continental mafic alkaline rocks (e.g., Janney *et al.*, 2002).

Results are discussed first for Sr-Nd isotope co-variations, then for co-variations between the three Pb isotope ratios, and finally variations between  $^{206}\text{Pb}/^{204}\text{Pb}$  and Sr and Nd isotope ratios. In all these sections, a comparison is made with comparable mafic alkaline rocks from intra-plate and rift tectonic settings.

### 1.6.1. Sr-Nd isotopic co-variations in the Namaqualand melilitites.

Figure 47 shows age-corrected  $^{87}\text{Sr}/^{86}\text{Sr}$  isotope ratios plotted versus  $\epsilon\text{Nd} (t)$  (i.e., age-corrected  $^{143}\text{Nd}/^{144}\text{Nd}$  values reported relative to the chondritic uniform reservoir (Bouvier *et al.*, 2008) for the Namaqualand melilitites. Nearly all of the Namaqualand samples fall within a narrow range of composition,  $^{87}\text{Sr}/^{86}\text{Sr}_i = 0.7031$  to  $0.7034$  (for leached samples) and  $\epsilon\text{Nd} (t) = +3.1$  to  $+3.8$ . The only locality that extends outside of this range is WAT, with  $^{87}\text{Sr}/^{86}\text{Sr}$  of up to  $0.70353$  and  $\epsilon\text{Nd} (t)$  down to  $+1.62$  which is unexpectedly within the field of south African Group 1 kimberlites.

The Namaqualand melilitites have Sr and Nd isotope ratios that overlap with those for southern African group 1 kimberlites, which extend to higher  $^{87}\text{Sr}/^{86}\text{Sr}_i$  ( $\approx 0.7054$ ) and lower  $\epsilon\text{Nd} (t)$  values ( $\approx -1$ ) than the melilitites (Figure 47). The Namaqualand melilitites overlap slightly with the HIMU-type ocean island basalts (e.g., from St. Helena Is. (South Atlantic) and Mangaia and Tubuai (Austral chain, South Pacific)), lying at the low  $\epsilon\text{Nd}$ , high  $^{87}\text{Sr}/^{86}\text{Sr}$  end of the small HIMU OIB field.

This partly overlaps with the small dataset obtained for the Namaqualand melilitites (Biesiesfontein only) by Rogers *et al.* (1992) on un-leached samples. Some of the Namaqualand melilitites share the same Sr and Nd isotope compositions Rogers *et al.* (1992) obtained on a smaller number of melilitites pipes spanning a range of  $\epsilon\text{Nd} (t)$  values of  $+2.6$  to  $+3.8$ , very similar to the main group of Namaqualand melilitites from this study, but with a slightly wider range of initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values, of  $0.7032$  to  $0.7038$ .

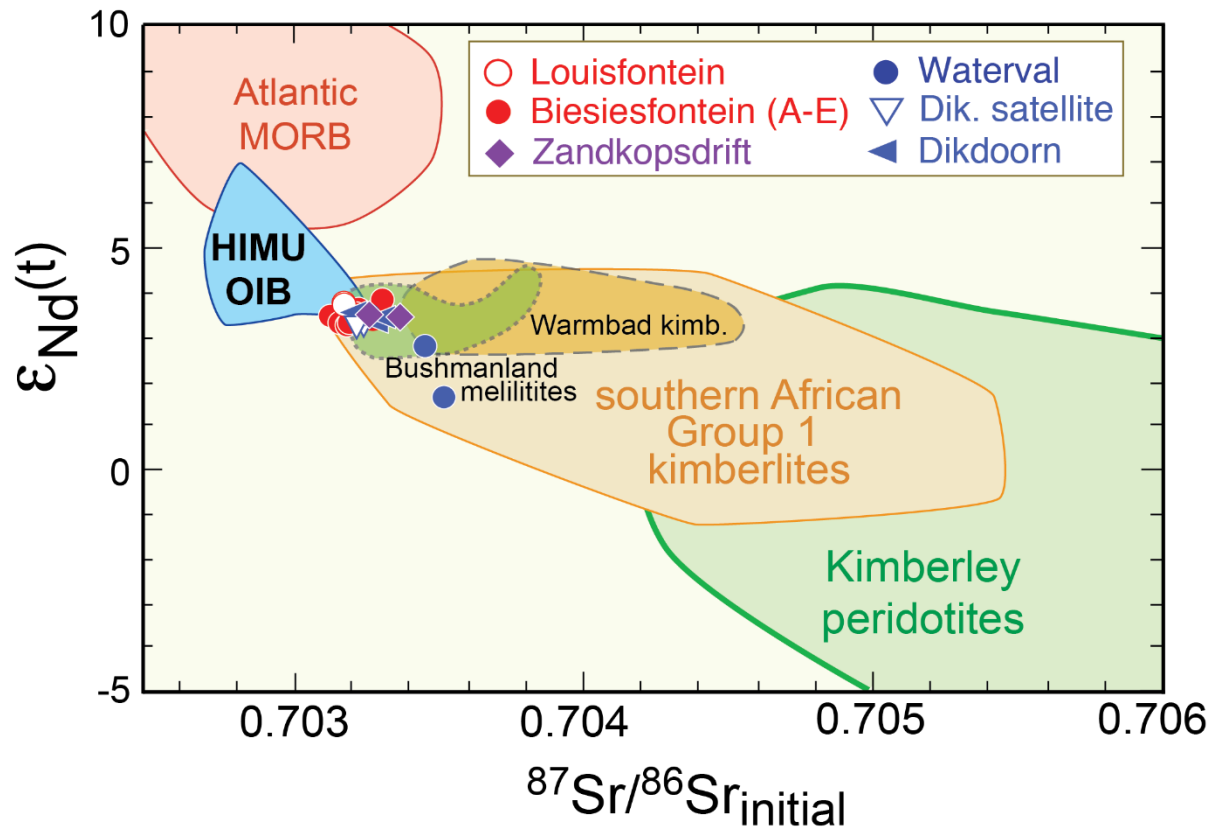


**Figure 47.** Plot of  $^{87}\text{Sr}/^{86}\text{Sr}_i$  versus  $\varepsilon_{\text{Nd}}(t)$  data for the Namaqualand samples compared to global examples of important related rock types. The Bushmanland and Warmbad melilitite data was from Janney *et al.* (2017). The kimberlitic field data was from Kramers, (1977), Kramers *et al.* (1981), Smith (1983), Nowell *et al.* (2004) and Becker & le Roex (2006). The Kimberley peridotite data is from Hawkesworth *et al.* (1990). The Atlantic MORB ocean island basalt data was obtained from the PETDB, 2018 and GeoROC database 2018.

### 5.5.1 *Pb isotopic results for the Namaqualand melilitites.*

Figure 48 shows plots of  $^{206}\text{Pb}/^{204}\text{Pb}_i$  vs.  $^{207}\text{Pb}/^{204}\text{Pb}_i$  and  $^{206}\text{Pb}/^{204}\text{Pb}_i$  vs.  $^{208}\text{Pb}/^{204}\text{Pb}_i$  for the Namaqualand melilitite samples. They span a fairly wide range of Pb isotope compositions, extending from radiogenic values nearly identical to OIB from the islands of Tubuai and St. Helena (e.g.,  $^{206}\text{Pb}/^{204}\text{Pb}_i$  of up to 21.2), to less radiogenic values comparable to enriched Atlantic MORB and southern African Group 1 kimberlites (i.e.,  $^{206}\text{Pb}/^{204}\text{Pb}_i$  down to 19.4). There is a large degree of overlap between the Pb isotopic compositions of the Namaqualand melilitites with both the Bushmanland melilitites and the Warmbad kimberlites (Described in Chapter 2.1; 2.2), and all extend to similarly un-radiogenic Pb isotopic compositions (of  $^{206}\text{Pb}/^{204}\text{Pb}_i$  19.0 to 19.5). However, the Namaqualand melilitites extend to much more radiogenic Pb isotope compositions than either the Warmbad kimberlites or the Bushmanland melilitites (e.g., with  $^{206}\text{Pb}/^{204}\text{Pb}_i$  values of up to 19.9 and 20.3, respectively). It may be significant that this variation in Pb isotopes correlates negatively with lithospheric thickness as the Namaqualand melilitites are found on the continental margin while the Bushmanland and Warmbad melilitites are found more inland with a greater crustal thickness (e.g., the

highest radiogenic Pb isotope compositions of melilitites or kimberlites are found on the thinnest lithosphere).

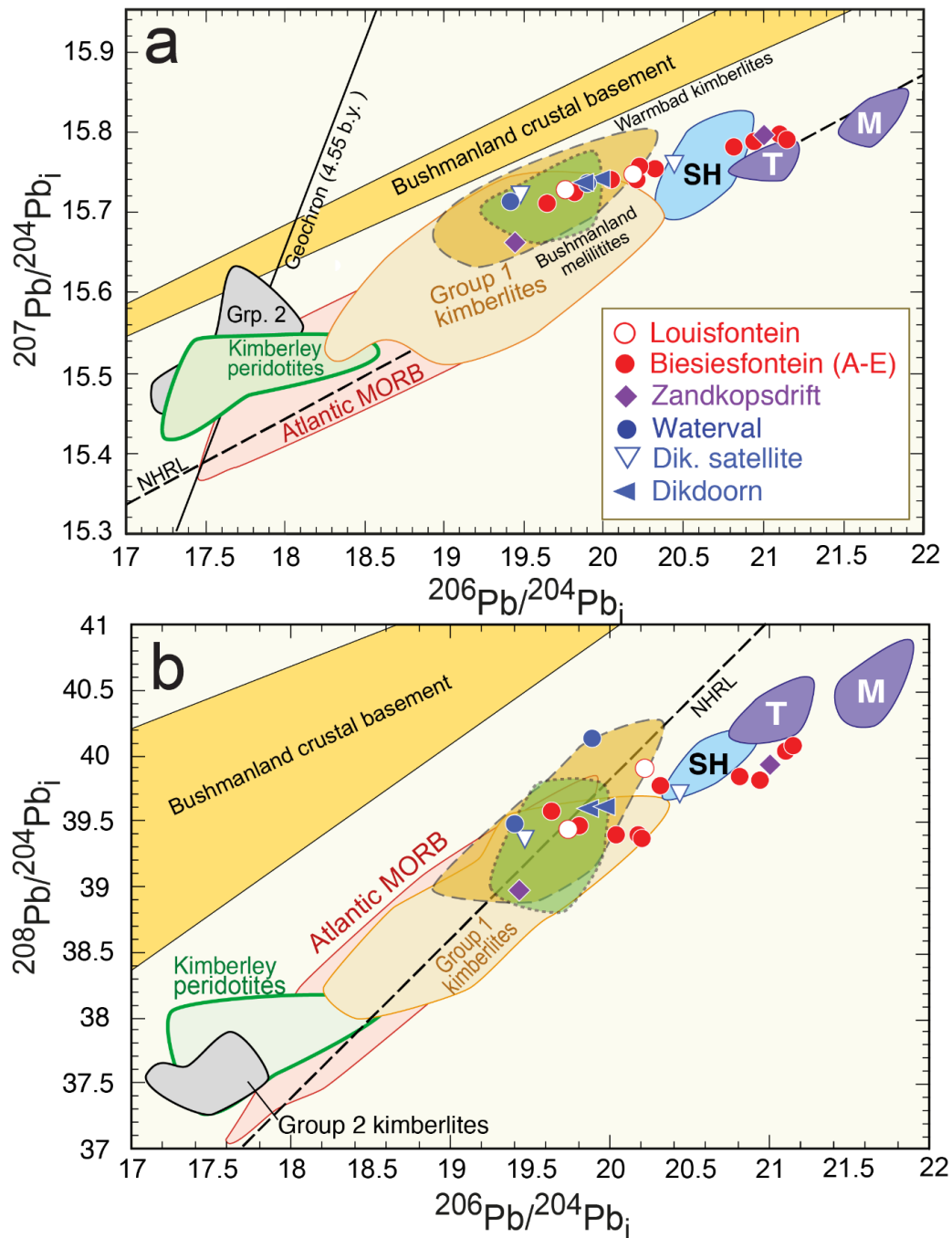


**Figure 48.** Plots of initial Pb isotope composition of the Namaqualand melilitites (a)  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{207}\text{Pb}/^{204}\text{Pb}$  (b)  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{208}\text{Pb}/^{204}\text{Pb}$ . Also shown are fields for the Bushmanland melilitites and Warmbad kimberlites, Atlantic MORB, southern African kimberlites, metasomatized peridotites from Kimberley and HIMU-type ocean island basalts. Abbreviations: SH, St. Helena, M, Mangaia, T, Tubuai. The data sources from Figure 47 were used as well as data from Fraser and Hawkesworth (1992) and Collerson *et al.* (2010) for Pb isotope data for South African Group 1 and Group 2 kimberlites. The values obtained for the Bushmanland crustal rocks are measured values as opposed to initial values from Reid *et al.* (1997).

All of the NBW province igneous rocks display significantly more radiogenic Pb isotopic compositions than metasomatized southern African peridotite xenoliths (e.g., Hawkesworth *et al.*, 1990) and Group 2 kimberlites (e.g., Smith, 1983). The NBW province igneous rocks are characterised by high  $^{207}\text{Pb}/^{204}\text{Pb}_i$  and  $^{208}\text{Pb}/^{204}\text{Pb}_i$  for a given  $^{206}\text{Pb}/^{204}\text{Pb}_i$  value compared to oceanic basalts, kimberlites, and melilitites (Reid *et al.*, 1997). Similarly, they do not display noticeable Pb isotopic similarities to the regional Namaqualand-Bushmanland crustal basement (Reid *et al.*, 1997; Fig. 15), although given the very wide range of Pb isotope compositions measured in this crust, a small contribution cannot be ruled out.

### 5.5.2 ***Co-variations of $^{206}\text{Pb}/^{204}\text{Pb}_i$ with Sr and Nd isotope ratios.***

The initial  $^{206}\text{Pb}/^{204}\text{Pb}$  values of the Namaqualand melilitites display roughly negative and positive correlations with initial  $^{87}\text{Sr}/^{86}\text{Sr}$  and  $\epsilon\text{Nd}(t)$ , respectively in Figure 49. As with Sr-Nd and Pb-Pb isotope variations, there is a large degree of overlap between the Namaqualand melilitites and Bushmanland melilitites and Warmbad kimberlites in  $^{206}\text{Pb}/^{204}\text{Pb}$ - $^{87}\text{Sr}/^{86}\text{Sr}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$ - $\epsilon\text{Nd}(t)$ , with these latter two groups of igneous rocks having, on average, slightly lower  $^{206}\text{Pb}/^{204}\text{Pb}_i$  and higher  $^{87}\text{Sr}/^{86}\text{Sr}_i$  values than the Namaqualand melilitites.

There is little overlap with southern African Group 1 kimberlites, as these have significantly lower  $^{206}\text{Pb}/^{204}\text{Pb}_i$  at a given  $^{87}\text{Sr}/^{86}\text{Sr}$  or  $\epsilon\text{Nd}(t)$  value compared to the Namaqualand samples. Similarly, there is no overlap with the metasomatized southern African peridotite xenoliths and Group 2 kimberlites (the latter of which have very high  $^{87}\text{Sr}/^{86}\text{Sr}$  and low  $\epsilon\text{Nd}(t)$  values such that they do not even plot on Figure 49). However, the Namaqualand melilitites closely approach the composition of HIMU-type ocean island basalts, although they tend to have slightly higher  $^{87}\text{Sr}/^{86}\text{Sr}$  and slightly lower  $\epsilon\text{Nd}(t)$  than HIMU OIB for a given  $^{206}\text{Pb}/^{204}\text{Pb}$  value.

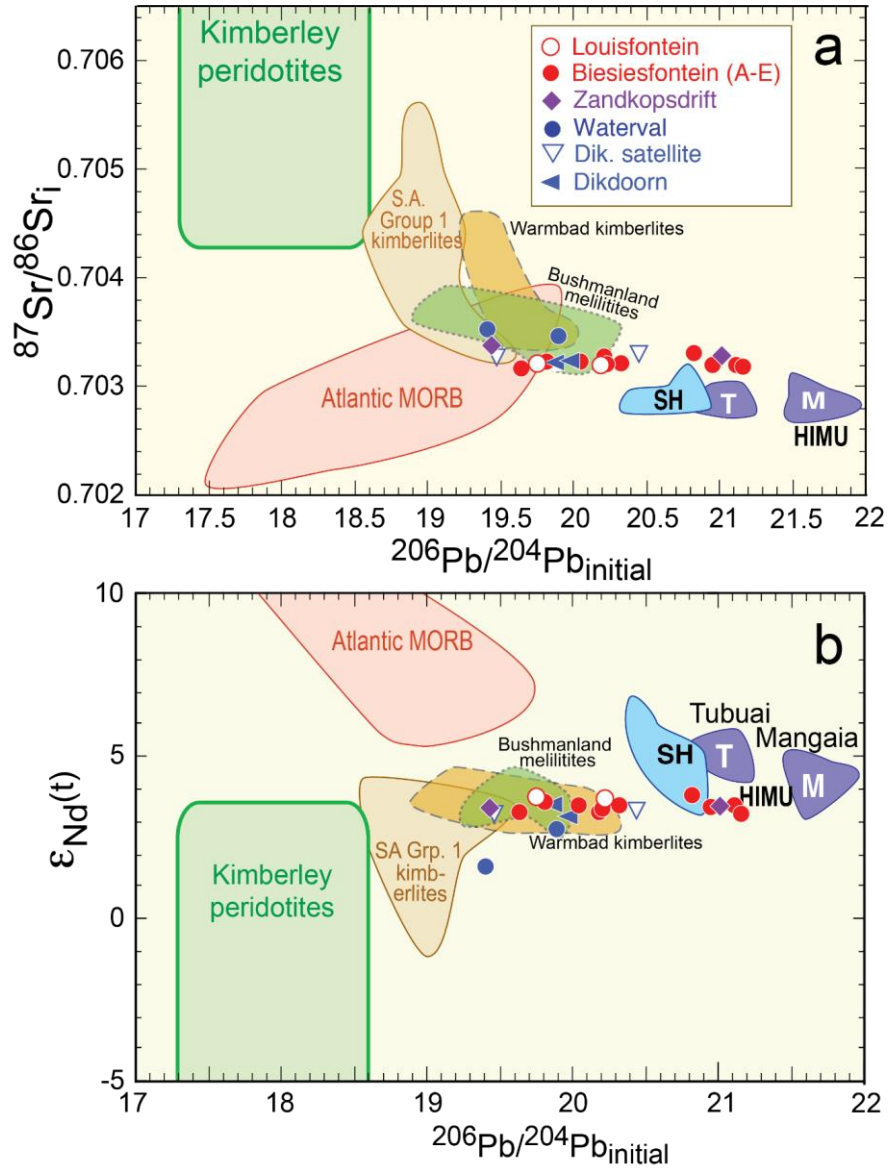


**Figure 49.** Plots of  $^{206}\text{Pb}/^{204}\text{Pb}_i$  versus (a)  $^{87}\text{Sr}/^{86}\text{Sr}_i$  and (b)  $\epsilon_{\text{Nd}}(t)$  for the Namaqualand samples compared to related igneous rocks such as kimberlites, MORB and OIB. The data for the Namaqualand samples measured in this study extend further towards HIMU and the OI compositions for Tubuai and Mangaia however, some of the samples overlap with the Warmbad kimberlites, as well some of the SA Group 1, kimberlites and Bushmanland melilitites. The data sources used for these data fields were the same as those used in Figure 47 and Figure 48.

## 6. OLIVINE OXYGEN ISOTOPE ANALYSIS:

Olivine crystals from these Namaqualand melilitites (Table 11) have  $\delta^{18}\text{O}_{\text{SMOW}}$  values between 5.22 and 4.22 ‰. These range from typical mantle values (4.9 to 5.5 ‰; Matthey *et al.*, 1994) to values that are significantly isotopically lighter. The olivines with the lowest  $\delta^{18}\text{O}$  values come from three pipes (BIES-C, -D and -E with  $\delta^{18}\text{O}$  minima of 4.3, 4.2 and 4.7 ‰, respectively) located on Farm Biesiesfontein, all of which are located within the Early Cretaceous Koegel Fontein Igneous Complex. Melilitites from the nearby Louisfontein pipe, located outside and to the southeast of the Koegel Fontein complex also yielded olivine crystals with  $\delta^{18}\text{O}$  values extending very slightly outside of the mantle range (4.8 to 5.1‰). However, the lowest value (4.8‰) for this locality does not lie below the established mantle range, given the analytical uncertainty of  $\pm 0.16\text{‰}$ .

**Table 11. Oxygen isotope data for olivine phenocrysts from Namaqualand and Bushmanland.**

| Pipes within Koegel Fontein complex |         |    |                                      | Pipes outside Koegel Fontein complex |        |    |                                      |
|-------------------------------------|---------|----|--------------------------------------|--------------------------------------|--------|----|--------------------------------------|
| PIPE                                | Sample  | *# | $\delta^{18}\text{O}_{\text{VSMOW}}$ | PIPE                                 | Sample | *# | $\delta^{18}\text{O}_{\text{VSMOW}}$ |
| BIESA                               | BIES-11 | 2  | 5.08                                 | Dikdoorn                             | DIK-11 | 1  | 5.18                                 |
| BIESA                               | BIESA-2 | 1  | 5.18                                 | Dikdoorn                             | DIK-13 | 1  | 5.06                                 |
| BIESB                               | BIESB-3 | 3  | 5.22                                 | Dikdoorn satellite                   | DSAT-1 | 1  | 5.11                                 |
| BIESB                               | BIESB-1 | 1  | 5.08                                 | Dikdoorn satellite                   | DSAT-1 | 1  | 5.12                                 |
| BIESC                               | BIESC-1 | 11 | 4.34                                 | Dikdoorn satellite                   | DSAT-4 | 3  | 4.90                                 |
| BIESC                               | BIESC-1 | 1  | 4.57                                 | Louisfontein                         | LOU-3  | 1  | 4.99                                 |
| BIESC                               | BIESC-2 | 1  | 4.55                                 | Louisfontein                         | LOU-2  | 1  | 5.05                                 |
| BIESC                               | BIESC-2 | 1  | 4.51                                 | Louisfontein                         | LOU-4  | 1  | 4.86                                 |
| BIESC                               | BIESC-2 | 1  | 5.01                                 | Waterval                             | WAT-1  | 3  | 5.06                                 |
| BIESC                               | BIESC-3 | 1  | 4.75                                 | Waterval                             | WAT-2  | 3  | 5.14                                 |
| BIESC                               | BIESC-3 | 1  | 4.79                                 | <b>Bushmanland pipes**</b>           |        |    |                                      |
| BIESD                               | BIESD-1 | 1  | 4.22                                 | Zwartheuwel                          | ZH-1   | ?  | 5.14                                 |
| BIESD                               | BIESD-1 | 1  | 4.95                                 | Bruinkop Pipe B                      | BKB-10 | ?  | 5.24                                 |
| BIESE                               | BIESE-3 | 1  | 5.13                                 | Wolkraal                             | WK-1   | ?  | 5.17                                 |
| BIESE                               | BIESE-3 | 1  | 4.66                                 | Hoedkop                              | HO-5   | ?  | 5.23                                 |
|                                     |         |    |                                      | Spioenkop                            | SP-4   | ?  | 5.25                                 |

*Replicate sample names indicates separate analyses on grains from the same sample.*

*\* # indicates the number of crystals analyzed together per analysis.*

*\*\* Data from Day *et al.*, 2014.*

A previous oxygen isotope study of olivines from the Bushmanland region shows that these have values of between 5.14 and 5.25 ‰ (Day *et al.*, 2014) which are close to those of olivines from mantle peridotite nodules ( $5.18 \pm 0.28 \text{‰}$ ; Matthey *et al.*, 1994).

Some of the samples (BIESC-1, BIESC-2 and BIESD-1) from the Biesiesfontein C and D pipes have among the lowest reported  $\delta^{18}\text{O}$  values for olivine from mantle-derived magmas (e.g., Matthey *et al.*, 1994; Eiler, 2001). It is notable that these pipes were emplaced within the Koegel Fontein Igneous Complex which is also notable for having exceptionally low  $\delta^{18}\text{O}$  values in both the igneous rocks and the surrounding hydrothermally altered country rock gneisses (e.g., Curtis *et al.*, 2013). Louisfontein,

which is located fairly nearby, to but still outside of, the Koegel Fontein complex, has one sample that extends slightly outside the "mantle"  $\delta^{18}\text{O}$  range, however, is within the analytical error included ( $2\sigma$  value of 0.16 ‰).

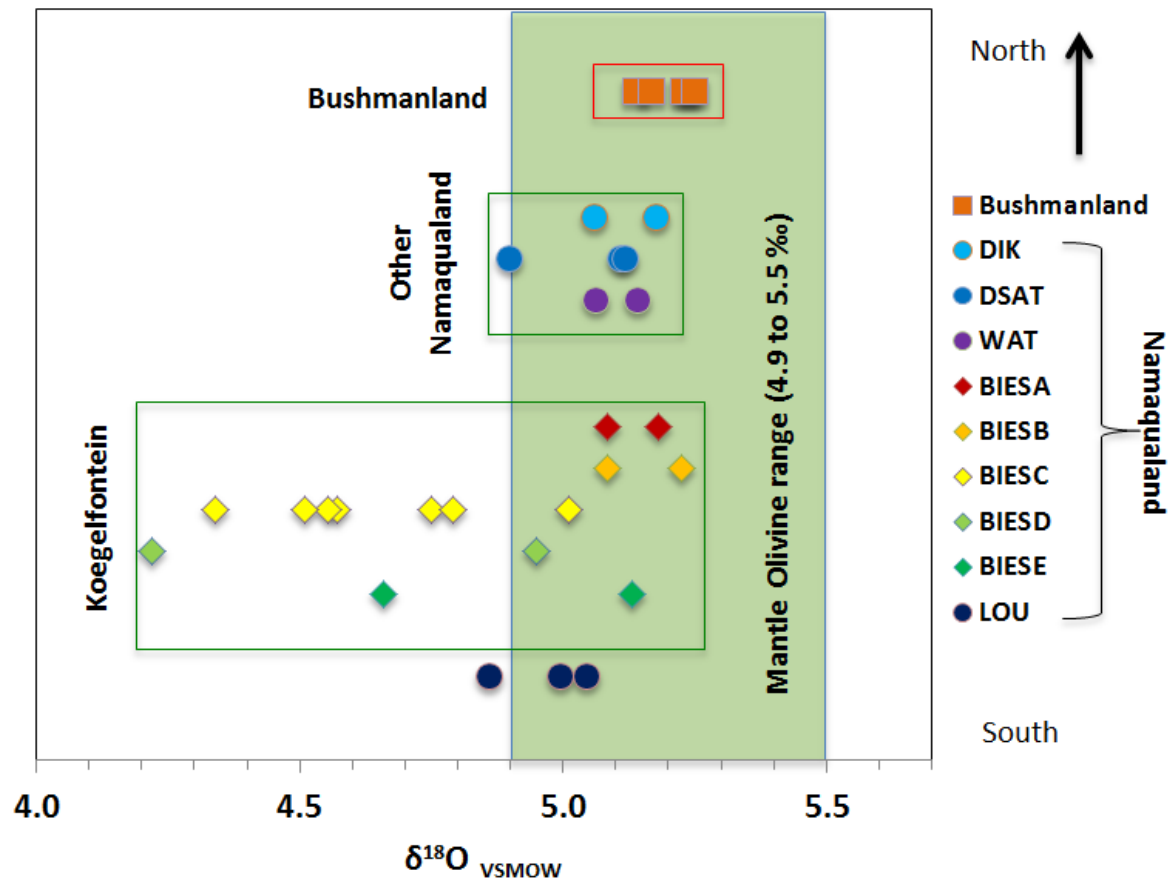


**Figure 50.** Oxygen isotope results for olivine grains from Namaqualand collected in this study and Bushmanland olivine data presented by Day *et al.* (2014). The oxygen isotope data are arranged according to the approximate geographic positions of the pipes from North (top) to South (bottom). The green box shows the expected compositional range for mantle olivine  $\delta^{18}\text{O}$  (Mattey *et al.*, 1994).

The oxygen results in Figure 50 are grouped by pipe to show the range of olivine  $\delta^{18}\text{O}$  values. The values are also shown in a histogram in Figure 51. Most of the values measured (57 %) are within the accepted mantle range of  $5.18 \pm 0.28$  ‰ (Mattey *et al.*, 1994), and 43% are below this range.

When considering the  $\delta^{18}\text{O}$  values for Namaqualand, it was considered if a relationship could be established between these  $\delta^{18}\text{O}$  results and earlier mentioned radiogenic isotopes. However, no correlation was found between the whole rock  $^{206}\text{Pb}/^{204}\text{Pb}$  and olivine  $\delta^{18}\text{O}$ . It was also noted that the localities with the largest ranges in olivine  $\delta^{18}\text{O}$  (e.g., BIES-C) do not also have the largest ranges in  $^{206}\text{Pb}/^{204}\text{Pb}$ .

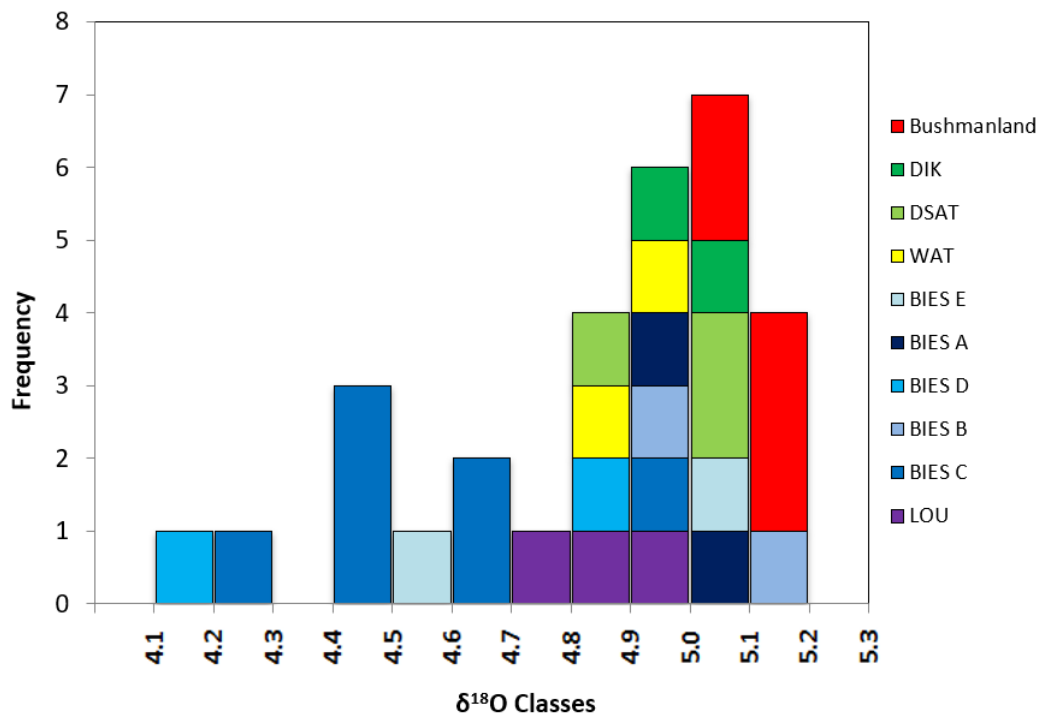


**Figure 51. Stacked histogram of the olivine oxygen isotope results colour coded by pipe for the Namaqualand cluster compared to the data from the Bushmanland pipes. Pipes are listed in order from north-east to south-west.**

## 7. DISCUSSION:

The purpose of this chapter is to interpret the mineral and whole-rock chemical and isotopic data obtained from the Namaqualand melilitites to better constrain the source and petrogenesis of these unusual igneous rocks. The objectives for this discussion include constraining the mineralogy of the mantle source and the degree of partial melting that formed these igneous rocks as well as an exploration of their relationship to the neighbouring Bushmanland melilitites, and the origin of the Namaqualand-Bushmanland-Warmbad igneous lineament. The previous, pioneering work of Moore (1979) focused mainly on the mineral chemistry of olivine in the melilitites, while this study will focus more on explaining their whole-rock major element, trace element and isotopic compositions.

An aspect of the Namaqualand melilitites that is of particular interest is the fact that they appear to be the product of variable, but generally fairly extensive, degrees of fractional crystallization. In this, they differ from the neighbouring Bushmanland melilitites and the vast majority of diatreme-hosted igneous rocks worldwide, which are mostly near-primary in composition. The Namaqualand melilitites have Mg# values as low as 45, indicating that they have experienced, in some cases, more than 50% fractional crystallization of an olivine-dominated mineral assemblage. This raises significant questions about the circumstances around how these igneous rocks came to have such differentiated compositions while having been emplaced as diatremes, which normally involves rapid ascent from mantle depths driven by the exsolution of carbon dioxide and other volatiles (Sparks, 2013). Additionally, there is the question of whether local continental crust was assimilated by the magmas during this fractionation and, if so, can this be used to provide insight into how and where this assimilation plus fractional crystallization occurred?

To better understand the petrogenesis of the Namaqualand melilitites, quantitative geochemical modelling of fractional crystallization is undertaken, as well as modelling of the mantle source composition, mineralogy and conditions of melting, informed by the composition, mineralogy, texture and mineral chemistry of the lavas. In addition, oxygen isotope data obtained on olivine separates is used to provide a crucial constraint on crustal assimilation within the Namaqualand melilitites due to the anomalously light  $\delta^{18}\text{O}$  signature of country rock in the vicinity of the mid-Cretaceous Koegelfontein intrusive complex through which some of the melilitites were emplaced.

The discussion will address the petrogenesis, potential source(s) and ultimate cause of the Namaqualand melilitite magmatism using a “top-down” approach, starting with fractionation history. For the sake of simplicity in the discussion below, the terms “Namaqualand melilitites” and “Bushmanland melilitites” are used to encompass relatively fresh olivine melilitites, olivine nephelinites and nephelinites from these pipe clusters. These terms also exclude the vesicular or volcanoclastic melilitite varieties recovered from the periphery of several of these pipes because these samples tend to have experienced a greater degree of alteration than the fresh, non-vesicular igneous rock found in the pipe interiors.

## 7.1. Fractional crystallization history of the Namaqualand melilitites.

The Namaqualand melilitites have relatively low Mg# values (45-71, average = 57.2), compared to both the neighbouring Bushmanland melilitites (67-76, average = 70.6; Moore, 1979; Janney *et al.*, 2017) and the Western Cape olivine melilitites (70 – 79, average = 74.5; Janney *et al.*, 2002). Moreover, because of the strongly SiO<sub>2</sub>-undersaturated nature of these magmas, this fractionation of olivine resulted in decreases in SiO<sub>2</sub> as well as MgO and Mg# (e.g., with SiO<sub>2</sub> contents for Namaqualand melilitites of 30 - 36 wt.%, (average = 32.4 wt.%) versus 32 – 40 wt.% (average = 35.6 wt.%) and 32 – 41 wt.% (average 35.7 wt.%) for the Bushmanland and Western Cape melilitites, respectively.

Rogers *et al.* (1992), based on whole-rock melilitite samples from Moore (1979), inferred that the low Mg# values and SiO<sub>2</sub> contents of the Namaqualand melilitites were a primary feature of their parent magmas (i.e., that they were derived from primary magmas with significantly lower SiO<sub>2</sub> than the Bushmanland melilitites) and they also proposed that the main compositional differences between the Namaqualand and Bushmanland melilitites were the result of smaller degrees of partial melting to generate the former, rather than greater extents of fractional crystallization. One factor that would have made this hypothesis more plausible is if the Fe<sup>2+</sup>/Mg partitioning between olivine and melt was strongly affected by the oxygen fugacity of the melt, as proposed by Moore and Erlank (1979). However, later work (e.g., Putirka *et al.*, 2007) has not supported the hypothesis that olivine Fe/Mg partitioning is highly sensitive to oxygen fugacity. Additionally, the discovery in the course of this research of a near-primary melilitite pipe from farm Waterval in the Namaqualand cluster (Mg# 70-71, MgO = 16.0-17.1, SiO<sub>2</sub> = 35.5-36.4), which is very similar in terms of major elements to Bushmanland melilitites, all clearly indicate that the Namaqualand melilitites were affected by significant fractional crystallization dominated by olivine.

Below, two approaches are used to constrain the fractionation history of the Namaqualand melilitites. The first approach assumes that olivine was the sole mineral in the fractionating assemblage and uses calculated equilibrium olivine compositions to iteratively correct the modelled composition. The second approach employs least-squares modelling to incorporate a wider range of minerals in the fractionating assemblage. It is acknowledged that both of these approaches are rather simplistic and likely to provide only rough constraints on fractionation history. Unfortunately, more realistic fractionation modelling, using codes such as pMELTS or Pele, was not feasible because these programs are not capable of dealing with the extremely strongly silica undersaturated (and often larnite-normative) magma compositions of the Namaqualand melilitites.

### 7.1.1 *Modelling fractional crystallization with olivine alone.*

This simple modelling approach uses Fe/Mg equilibria between olivine and liquid to calculate the composition of olivine in equilibrium with each sample's measured major element composition.

This is expressed as (in atomic units):  $(\text{Fe}^{2+}/\text{Mg})_{\text{ol}} = (\text{Fe}^{2+}/\text{Mg})_{\text{liq}} * 0.3 \pm 0.03$  (Roedder and Emslie, 1970). Olivine in Fe/Mg equilibrium with the magma is added in increments of 2% (i.e., the composition of a mixture of 2% equilibrium olivine and 98% of the sample ("melt") composition is calculated). This operation is repeated iteratively until an Mg# of 73 for the melt composition is reached, which is the assumed primary magma composition (i.e., in equilibrium with olivine of composition Fo91). To perform this modelling, a  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio of 0.15 ( $\text{Fe}^{3+}/\Sigma\text{Fe} \approx 0.13$ ) in the melilitites is assumed.

This model has the advantage that olivine which is in Fe/Mg equilibrium with the magma is used for quantifying the amount of fractionation and correcting the magma composition. However, it has a major disadvantage in that it explicitly assumes that olivine is the only fractionating phase, which is likely incorrect. However, by comparing the olivine fractionation-corrected compositions of the Namaqualand melilitites with those for the Bushmanland melilitites, the extent of a mismatch for each major element can be gauged and this can be used to constrain which other minerals were likely important in the fractionating assemblage. If olivine is indeed the main mineral in the fractionating assemblage, such an approach should be effective at correcting the compositions of the Namaqualand melilitites to ones similar to the near-primary Bushmanland melilitites. Correcting the Mg# values of every Namaqualand melilitite sample to a value of 73 requires the addition of between 6 and 60% equilibrium olivine (Table 12).

**Table 12. Original Mg# values and percentage of cumulative equilibrium olivine fractionation needed to explain the compositions of the Namaqualand melilitites assuming they formed from primary magmas with an Mg number of 73.**

| Namaqualand Melilitites |             |                         |             |             |                         |             |             |                         |
|-------------------------|-------------|-------------------------|-------------|-------------|-------------------------|-------------|-------------|-------------------------|
| Sample name             | Initial Mg# | % Olivine fractionation | Sample name | Initial Mg# | % Olivine fractionation | Sample name | Initial Mg# | % Olivine fractionation |
| DIK-10                  | 60          | 34                      | ZAND-1*     | 57          | 38                      | BIESC-1     | 62          | 30                      |
| DIK-11                  | 58          | 38                      | ZAND-2*     | 52          | 48                      | BIESC-2     | 60          | 34                      |
| DIK-12                  | 60          | 34                      | ZAND-4*     | 56          | 42                      | BIESC-3     | 62          | 30                      |
| DIK-13                  | 59          | 36                      | ZAND-7*     | 56          | 40                      | BIESD-1     | 50          | 58                      |
| DSAT-1                  | 45          | 58                      | BIES-10     | 58          | 40                      | BIESD-2     | 50          | 58                      |
| DSAT-2                  | 48          | 56                      | BIES-11     | 58          | 40                      | BIESD-3     | 49          | 60                      |
| DSAT-3A                 | 49          | 54                      | BIESA-1     | 58          | 40                      | BIESD-4     | 50          | 58                      |
| DSAT-3B                 | 48          | 56                      | BIESA-2     | 58          | 40                      | BIESE-1     | 49          | 60                      |
| DSAT-4                  | 51          | 50                      | BIESB-1     | 65          | 22                      | BIESE-2     | 50          | 60                      |
| WAT-1                   | 70          | 10                      | BIESB-2     | 64          | 24                      | BIESE-3     | 49          | 58                      |
| WAT-2                   | 71          | 6                       | BIESB-3     | 64          | 24                      | LOU-2       | 57          | 40                      |
|                         |             |                         |             |             |                         | LOU-3       | 59          | 36                      |
|                         |             |                         |             |             |                         | LOU-4       | 58          | 38                      |

*\*Samples ZAND-1, -2, -4 and -7 are from Ogungbuyi et al. (2022).*

In contrast, the Bushmanland pipes only require up to 10% olivine fractionation to bring their Mg# values up to 73, and nearly half of these samples have Mg# in excess of 73. This means that they likely experienced up to 16% olivine accumulation.

**Table 13. Fractionation corrected major element data for Namaqualand melilitites obtained by iterative addition of equilibrium olivine to reach an Mg number of ~73.**

| Sample ID | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO <sub>tot</sub> | MnO | MgO  | CaO  | Na <sub>2</sub> O | K <sub>2</sub> O | P <sub>2</sub> O <sub>5</sub> | Total |
|-----------|------------------|------------------|--------------------------------|--------------------|-----|------|------|-------------------|------------------|-------------------------------|-------|
| DIK-10    | 34.1             | 4.9              | 4.4                            | 16.4               | 0.2 | 22.1 | 12.4 | 1.2               | 2.6              | 1.7                           | 100   |
| DIK-11    | 35.1             | 5.1              | 4.5                            | 16.6               | 0.2 | 22.4 | 11.9 | 1.0               | 1.7              | 1.5                           | 100   |
| DIK-12    | 34.1             | 4.9              | 4.4                            | 16.3               | 0.2 | 22.1 | 12.4 | 1.5               | 2.3              | 1.7                           | 100   |
| DIK-13    | 34.5             | 5.0              | 4.5                            | 16.4               | 0.2 | 22.2 | 11.8 | 1.0               | 2.7              | 1.6                           | 100   |
| DSAT-1    | 38.0             | 4.2              | 5.5                            | 16.6               | 0.1 | 23.2 | 9.3  | 1.3               | 0.7              | 1.0                           | 100   |
| DSAT-2    | 37.7             | 4.3              | 5.3                            | 17.1               | 0.2 | 23.7 | 8.6  | 1.3               | 0.7              | 0.9                           | 100   |
| DSAT-3A   | 37.7             | 4.4              | 5.4                            | 17.0               | 0.2 | 23.5 | 8.9  | 1.3               | 0.8              | 0.9                           | 100   |
| DSAT-3B   | 37.7             | 4.3              | 5.4                            | 17.1               | 0.2 | 23.7 | 8.6  | 1.3               | 0.8              | 0.9                           | 100   |
| DSAT-4    | 37.3             | 4.3              | 5.4                            | 17.0               | 0.2 | 23.3 | 9.6  | 1.2               | 0.7              | 1.1                           | 100   |
| WAT-1     | 38.3             | 4.0              | 6.0                            | 14.4               | 0.2 | 19.5 | 12.4 | 2.0               | 1.6              | 1.5                           | 100   |
| WAT-2     | 37.3             | 4.1              | 5.8                            | 14.7               | 0.2 | 19.6 | 12.7 | 2.1               | 1.8              | 1.6                           | 100   |
| ZAND-1    | 35.5             | 5.4              | 4.5                            | 16.1               | 0.2 | 22.0 | 11.2 | 1.6               | 2.1              | 1.3                           | 100   |
| ZAND-2    | 36.0             | 5.4              | 4.5                            | 16.2               | 0.2 | 22.5 | 10.2 | 1.8               | 1.9              | 1.2                           | 100   |
| ZAND-4    | 36.7             | 5.6              | 4.6                            | 16.8               | 0.2 | 22.9 | 7.8  | 1.3               | 2.5              | 1.4                           | 100   |
| ZAND-7    | 35.6             | 5.2              | 4.6                            | 16.4               | 0.2 | 22.2 | 11.0 | 1.5               | 2.0              | 1.3                           | 100   |
| BIESE-1   | 36.7             | 4.8              | 4.5                            | 17.9               | 0.2 | 25.1 | 8.4  | 0.9               | 0.6              | 1.0                           | 100   |
| BIESE-2   | 36.4             | 4.7              | 4.5                            | 18.5               | 0.2 | 25.6 | 8.0  | 0.6               | 0.6              | 0.8                           | 100   |
| BIESE-3   | 36.8             | 4.6              | 4.7                            | 17.8               | 0.2 | 24.8 | 8.1  | 1.1               | 0.9              | 1.0                           | 100   |
| BIES-10   | 36.5             | 5.3              | 4.7                            | 17.5               | 0.2 | 23.6 | 9.1  | 0.7               | 1.6              | 1.0                           | 100   |
| BIES-11   | 36.5             | 5.3              | 4.7                            | 17.3               | 0.2 | 23.6 | 8.9  | 0.8               | 1.8              | 1.0                           | 100   |
| BIESA-1   | 35.9             | 5.4              | 4.5                            | 17.4               | 0.2 | 23.8 | 8.9  | 0.6               | 2.2              | 1.0                           | 100   |
| BIESA-2   | 36.4             | 5.2              | 4.7                            | 17.4               | 0.2 | 23.7 | 8.9  | 0.7               | 1.8              | 1.0                           | 100   |
| BIESD-1   | 36.2             | 4.7              | 4.5                            | 18.1               | 0.2 | 25.3 | 8.6  | 0.9               | 0.7              | 0.9                           | 100   |
| BIESD-2   | 36.1             | 4.7              | 4.5                            | 18.2               | 0.2 | 25.3 | 8.3  | 1.0               | 0.7              | 0.9                           | 100   |
| BIESD-3   | 36.5             | 4.8              | 4.5                            | 18.2               | 0.2 | 25.2 | 8.4  | 0.8               | 0.5              | 0.9                           | 100   |
| BIESD-4   | 36.3             | 4.7              | 4.6                            | 18.3               | 0.2 | 25.4 | 7.9  | 1.0               | 0.6              | 1.0                           | 100   |
| BIESB-1   | 34.9             | 4.9              | 5.0                            | 16.0               | 0.2 | 21.2 | 12.5 | 1.0               | 2.6              | 1.7                           | 100   |
| BIESB-2   | 35.9             | 5.0              | 5.2                            | 16.0               | 0.2 | 21.6 | 11.7 | 1.0               | 1.7              | 1.6                           | 100   |
| BIESB-3   | 34.9             | 4.9              | 5.0                            | 15.9               | 0.2 | 21.6 | 12.6 | 1.0               | 2.2              | 1.7                           | 100   |
| BIESC-1   | 36.1             | 4.0              | 5.3                            | 16.1               | 0.2 | 22.2 | 11.2 | 2.0               | 1.5              | 1.3                           | 100   |
| BIESC-2   | 35.5             | 4.1              | 5.3                            | 16.4               | 0.2 | 22.3 | 11.3 | 1.9               | 1.5              | 1.4                           | 100   |
| BIESC-3   | 36.0             | 4.0              | 5.2                            | 16.4               | 0.2 | 22.4 | 11.3 | 1.8               | 1.2              | 1.3                           | 100   |
| LOU-2     | 35.4             | 4.9              | 5.0                            | 16.5               | 0.2 | 22.8 | 11.4 | 1.0               | 1.6              | 1.2                           | 100   |
| LOU-3     | 34.7             | 4.6              | 5.0                            | 15.8               | 0.2 | 21.8 | 12.5 | 1.6               | 2.2              | 1.4                           | 100   |
| LOU-4     | 35.2             | 4.9              | 5.0                            | 16.5               | 0.2 | 22.3 | 11.2 | 1.4               | 2.2              | 1.2                           | 100   |

*Localities list approximately from north to south. Note that all fractionation-corrected compositions are normalized volatile-free. \*Samples ZAND-1, -2, -4 and -7 are from Ogungbuyi et al. (2022).*

There is no coherent regional variation and indeed two of the most distinct pipes in terms of the apparent extent of olivine fractionation, WAT (6-10%) and DSAT (50-58%), are located only a few kilometres from each other. Variation in olivine fractionation within individual pipes is 10% or less, but samples from most individual pipes vary by only 2-6%. Major element compositions of the Namaqualand melilitites corrected for olivine fractionation are given in Table 13, and these are plotted

in Figure 52. The major element compositions of the corrected Namaqualand melilitite compositions show a high degree of overlap with those of the (uncorrected) Bushmanland melilitites in plots of MgO versus SiO<sub>2</sub>, TiO<sub>2</sub>, MnO, CaO and Na<sub>2</sub>O, and slightly lesser overlap in plots versus Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O and P<sub>2</sub>O<sub>5</sub>, where the Namaqualand melilitites tend to display higher values for all of these oxides for a given MgO content. In the plot of MgO versus FeO<sup>total</sup>, the majority of fractionation-corrected Namaqualand melilitite data fall at higher FeO<sup>total</sup> contents as well as higher P and lower Ti than those of the Bushmanland melilitites. It is likely that the omission of magnetite as a fractionating phase is not the only attributing factor. If magnetite were included with olivine in the fractionating assemblage, this would make the fractionation-corrected compositions even more Fe-rich relative to the Bushmanland melilitites. In general, while the modelling in this section suggests that olivine was likely the dominant member of the fractionating assemblage, this assemblage likely included other minerals.

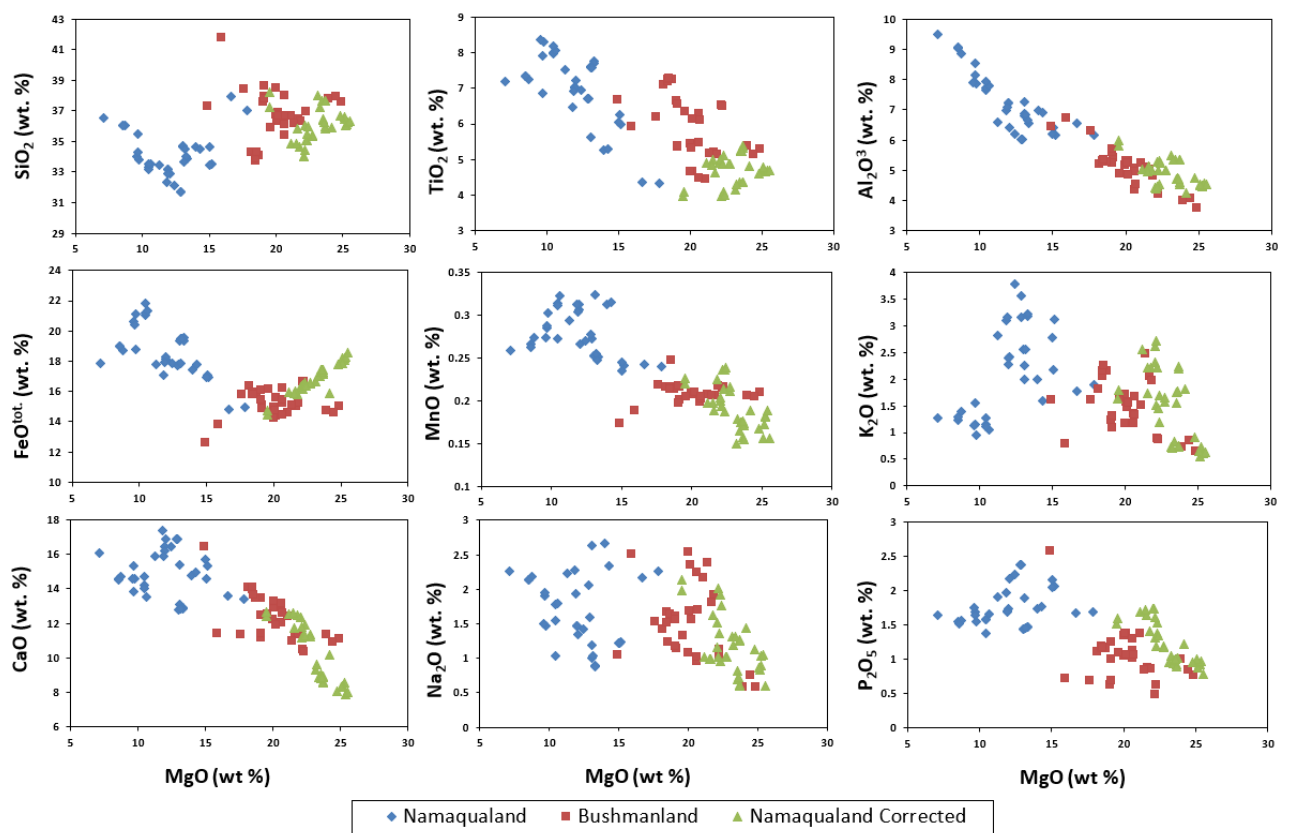


**Figure 52. Major oxides versus MgO (normalized volatile-free) for the Namaqualand melilitites (both uncorrected and corrected for olivine fractionation to Mg# = 73) compared to the results for the Bushmanland melilitites.**

### 7.1.2 Estimation of fractional crystallization assemblages and degrees using a least squares approach.

The other simple fractionation modelling approach used in this thesis is least squares. This model's fractional crystallization is a series of steps where, through crystallization, a parental magma is converted into a daughter magma plus an assemblage of minerals, the latter two of which together match the composition of the parent. This is done through a series of simple parallel mixing equations, one for each major oxide, with the composition of the parent magma composition on one side and a weighted average of the daughter magma and the fractionating phases on the other (see equation (2) below). MS Excel's Solver module calculates the mixing proportions that yield the smallest misfit for all major oxides.

The disadvantage of this modelling approach is that the compositions of the parent, daughter and all fractionating minerals are assumed rather than calculated. Additionally, the weighting assigned to each misfit is absolute, rather than proportional to the amount of the oxide present (i.e., a misfit of 0.1 out of a total of 40.0 wt.% for SiO<sub>2</sub> counts the same as a misfit of 0.1 out of a total of 0.2 wt.% for MnO), although different weightings can be assigned to different oxides if desired.

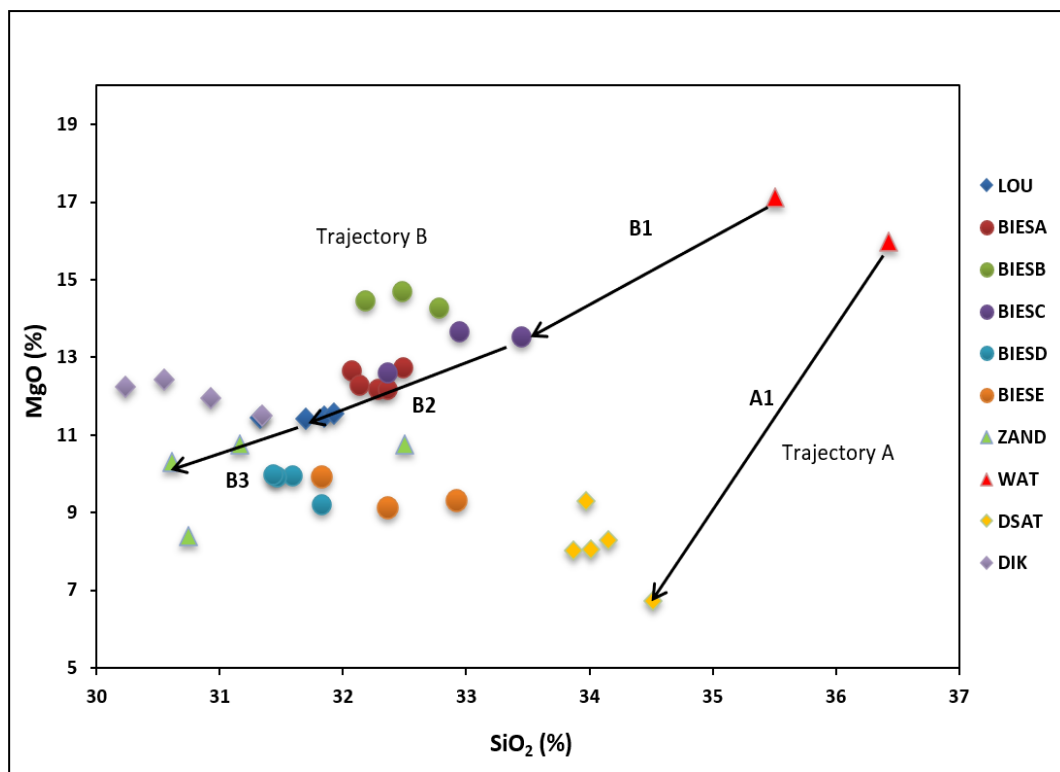


**Figure 53. Comparison of the major element data for the Namaqualand pipes showing least-squares fractionation modelling steps for the evolution of the magmas using the least squares model which follows two paths called Path A (Step A1) and Path B (Steps B1 to B3).**

The least squares fractionation model attempts to solve the equation for each major oxide:

$$(M^A)_{\text{Parent}} = (M^A)_{\text{Daughter}}X_1 + (M^A)_{\text{mineral (1)}}X_2 + (M^A)_{\text{mineral (2)}}X_3 + (M^A)_{\text{mineral (3)}}X_4 + \dots \quad (2)$$

Where  $M^A$  is major oxide A (e.g.,  $\text{SiO}_2$ ) in the parent, daughter, and minerals 1, 2, 3, etc., and the "X" terms are fractional values between zero and one such that the sum of all X terms is equal to unity. Value  $X_1$  (fraction of daughter magma remaining after the crystallization step) is equivalent to F in the fractional crystallization equation. Such equations are solved for every major oxide with the X terms being kept the same for all oxides in each step. The residuals for each oxide (i.e., the difference in value between the two sides of the equation (e.g.,  $\text{residual}^A = M^A_{\text{calculated parent}} - M^A_{\text{actual parent}}$ ) are squared and summed, with this term being called the residual sum of squares (RSS). It is this RSS value that, through iterative steps, the program attempts to minimise by changing the X values for the daughter and fractionating minerals. The closest approximation to the actual (assumed) parent composition (calculated as a mixture of daughter + fractionating minerals) is compared with the actual parent composition by the model, and the RSS value provides a means of evaluating the goodness-of-fit of this model (the smaller the RSS, the better the fit).

As can be seen in the  $\text{SiO}_2$  versus MgO plot in Figure 53 above, the Namaqualand melilitites do not form a single trend on variation diagrams, but rather appear to show an increase in compositional variability with increasing fractionation (i.e., the range of  $\text{SiO}_2$  values increases with decreasing MgO). To accommodate this variability, two modelling trajectories have been selected. Both start with samples from the Waterval (WAT) pipe, which is by far the least differentiated of the Namaqualand pipes. One trajectory, labelled Trajectory A, models the evolution of low-MgO sample DSAT-1 from the relatively primitive sample WAT-1 in a single step (Step A1). A second trajectory (B) models the formation of sample ZAND-7 (with relatively low Mg and also among the lower  $\text{SiO}_2$  contents of the Namaqualand melilitite samples) from sample WAT-2 in three steps (B1, B2 and B3), with samples BIESC-1 and LOU-3 as intermediates (see Figure 53 above). It is important to keep in mind that although the mineral compositions have been selected to be, as close as possible, in equilibrium with the selected parent and daughter compositions, such is not always the case and there may be some artefacts in the model due to minerals not being precisely in equilibrium with the parent or daughter compositions modelled. In the single step of model A1, deriving the DSAT-1 daughter from the WAT-1 parent magma composition resulted in a residual sum of squares (RSS) value of 0.11. For this step, the total amount of crystallization is 42% (with olivine making 40% of this, significantly less than the 58% fractionation of olivine alone calculated for DSAT-1 in the previous section). The other main minerals in the crystallizing assemblage are melilite (33.7%) and phlogopite (17.0%), with minor nepheline (4.3%), perovskite (3.2%), Fe-Ti oxides (2.3%) and clinopyroxene (0.4%).

**Table 14. Table with least squares calculations for Step A1, deriving DSAT-1 from WAT-1.**

|                          | Percentage   | Fraction     | SiO <sub>2</sub>   | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | FeO   | MnO  | MgO   | CaO   | Na <sub>2</sub> O | K <sub>2</sub> O | Total |
|--------------------------|--------------|--------------|--------------------|------------------|--------------------------------|-------|------|-------|-------|-------------------|------------------|-------|
| <b>Daughter:</b>         | %            |              | -----Weight %----- |                  |                                |       |      |       |       |                   |                  |       |
| <b>DSAT-1</b>            | 42.0         | 0.420        | 37.27              | 7.32             | 9.67                           | 18.22 | 0.26 | 7.26  | 16.39 | 2.31              | 1.29             | 100.0 |
| <b>olivine</b>           | 39.6         | 0.230        | 39.18              | 0.05             | 0.05                           | 17.71 | 0.32 | 42.35 | 0.34  | 0.00              | 0.00             | 100.0 |
| <b>clinopyroxene</b>     | 0.4          | 0.002        | 47.30              | 3.96             | 4.35                           | 6.62  | 0.11 | 13.72 | 23.67 | 0.25              | 0.01             | 100.0 |
| <b>melilite</b>          | 33.7         | 0.196        | 44.34              | 0.16             | 4.02                           | 4.99  | 0.20 | 9.35  | 33.75 | 2.99              | 0.19             | 100.0 |
| <b>Fe-Ti oxides</b>      | 3.6          | 0.021        | 0.00               | 15.76            | 1.48                           | 73.44 | 1.03 | 8.29  | 0.00  | 0.00              | 0.00             | 100.0 |
| <b>perovskite</b>        | 1.5          | 0.009        | 0.00               | 58.32            | 0.00                           | 1.26  | 0.00 | 0.00  | 39.90 | 0.41              | 0.10             | 100.0 |
| <b>nepheline</b>         | 4.3          | 0.025        | 40.86              | 0.05             | 34.67                          | 0.10  | 0.00 | 0.00  | 0.50  | 15.81             | 8.01             | 100.0 |
| <b>phlogopite</b>        | 17.0         | 0.099        | 42.16              | 4.58             | 11.61                          | 8.63  | 0.11 | 22.52 | 0.00  | 0.35              | 10.05            | 100.0 |
| <b>SUM</b>               | <b>100.0</b> | <b>1.000</b> |                    |                  |                                |       |      |       |       |                   |                  |       |
| <b>Parent Calculated</b> |              | %            | 38.59              | 4.40             | 6.90                           | 15.10 | 0.25 | 17.04 | 13.96 | 1.99              | 1.77             | 100.0 |
| <b>WAT-1</b>             |              | %            | 38.66              | 4.45             | 6.69                           | 15.09 | 0.25 | 16.97 | 13.87 | 2.21              | 1.82             | 100.0 |
| <b>RSS</b>               | <b>0.114</b> | residuals    | 0.07               | 0.04             | -0.21                          | -0.01 | 0.00 | -0.07 | -0.09 | 0.22              | 0.05             | -     |

*Notes: For modelling purposes, all rock and mineral compositions are normalized and reported free of volatiles, Cr<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub>. The olivine composition given is the average from sample DSAT-2, whereas the oxide composition is the average Fe-Ti oxide composition from WAT-2. The other mineral compositions are the average composition of these minerals from Namaqualand melilitites (Biesiesfontein and Zandkopsdrift) as reported by Boctor and Yoder (1983). In other models, the olivine and Fe-Ti oxide compositions used are from the parent or daughter, whichever gives the lowest RSS value. For steps B1, B2 and B3, the average melilite composition from LOU-3 is used for melilite.*

The least squares modelling (Table 15) provides a good indication that olivine is the most important, but not overwhelmingly dominant, a constituent of the crystallizing assemblage overall, and is particularly important early in the differentiation process. Clinopyroxene, melilite and Fe-Ti oxides become important later in the crystallisation process and phlogopite, nepheline and perovskite are present at minor to moderate levels in most crystallization steps but do not show systematic changes. However, a comparison of the fractionating assemblages and the actual mineral assemblages in the Namaqualand melilitite samples shows that there is little correspondence in detail. For example, Fe-Ti oxides are not absent in the samples used for Step B1, neither is clinopyroxene dominant in sample LOU-3 (Step B2) nor is olivine minor and melilite strongly dominant in sample ZAND-7 (Step B3)). It is, therefore, most likely that the least squares models are not precisely correct and they only provide a rough guide to the crystallizing assemblage.

**Table 15: Summary of the least squares modelling results.**

|                                          | Trajectory A | Trajectory B |         |         |
|------------------------------------------|--------------|--------------|---------|---------|
| Modelling step                           | Step A1      | Step B1      | Step B2 | Step B3 |
| Parent                                   | WAT-2        | WAT-2        | BIESC-1 | LOU-3   |
| Daughter                                 | DSAT-1       | BIESC-1      | LOU-3   | ZAND-7  |
| <b>Mixing Proportions (wt. %)</b>        |              |              |         |         |
| F (% melt remaining)                     | 42.4         | 60.8         | 41.7    | 22.0    |
| Crystals                                 | 57.6         | 39.2         | 58.3    | 78.0    |
| RSS*                                     | 0.11         | 0.02         | 0.72    | 1.59    |
| <b>Crystallizing Assemblages (wt. %)</b> |              |              |         |         |
| Olivine                                  | 39.6         | 40.2         | 16.2    | 6.6     |
| Clinopyroxene                            | 0.4          | 28.7         | 48.2    | 0.0     |
| Melilite                                 | 33.7         | 11.2         | 5.7     | 49.9    |
| Fe-Ti oxides                             | 3.6          | 0.0          | 18.2    | 19.8    |
| Perovskite                               | 1.5          | 2.0          | 0.0     | 2.6     |
| Nepheline                                | 4.3          | 6.1          | 11.6    | 7.3     |
| Phlogopite                               | 17.0         | 11.9         | 0.0     | 13.8    |
| Total                                    | 100          | 100          | 100     | 100     |

\*RSS is the residual sum of squares of residuals in the given modelling step.

The total amount of crystallization calculated from least squares model steps B1, B2 and B3 (i.e., from sample WAT-2 to ZAND-7) is equal to  $1 - F_{B1} \cdot F_{B2} \cdot F_{B3} = 0.945$  in fractional terms or 94.5% crystallization. This is unrealistically high given that the mineralogy and mineral proportions of these samples are fairly similar (see petrography table), as  $\approx 95\%$  fractional crystallization of an olivine melilitite, in reality, should yield a phonolite with minor olivine (at most) and dominant feldspathoids (e.g., Nosova *et al.*, 2021). This is another indication that these least squares models are inaccurate in detail and should only be used as a very rough guide.

## 7.2. Quantifying crustal assimilation in the Namaqualand melilitites.

The relatively evolved compositions of most Namaqualand melilitites suggest the possibility that their fractionation may have been accompanied by crustal assimilation, as these two processes are often closely related (DePaolo, 1981). As will be demonstrated below, there is little evidence for detectable crustal assimilation in the Namaqualand melilitites from conventional lithophile trace elements and isotope ratios. However, oxygen isotopes offer persuasive evidence that at least a very minor amount of assimilation of continental crust having an anomalously low  $\delta^{18}\text{O}$  value, did occur in some Namaqualand melilitites. For this reason, I start with this evidence and then move on to other types of data where the evidence for crustal assimilation is more equivocal.

The extent of crustal assimilation affecting the Namaqualand melilitites may be evaluated using three main strategies: (1) a comparison of oxygen isotope compositions in olivines from the

Namaqualand melilitites with those from other South African melilitites and southern African kimberlites. The anomalously light oxygen isotope composition of the crust in parts of Namaqualand (e.g., Curtis *et al.*, 2013) makes this potentially the most sensitive tracer of crustal assimilation in the melilitites. (2) a comparison of their Pb and Hf isotopic compositions to such crustal rocks, since crustal Pb isotope compositions tends to be distinct from those of recently mantle-derived rocks, and crustal rocks and small-volume mantle-derived rocks such as kimberlites often display very different senses of Hf-Nd isotope decoupling (e.g., Nowell *et al.*, 2004; Schmitz *et al.*, 2004, Chauvel *et al.*, 2014); and (3) a comparison of their elemental compositions to those of crustal rocks sampled during this study as well as to regional and global upper and lower crust from other studies (e.g., Schmitz *et al.*, 2004; Rudnick *et al.*, 2003), particularly focusing on major and trace elements that ideally should be sensitive to crustal assimilation (such as Pb and SiO<sub>2</sub>).

### 7.2.1 ***Constraints on crustal assimilation from oxygen isotopes in olivine separates.***

Oxygen isotope data in this study were obtained on olivine phenocrysts separated from Namaqualand melilitites. The data reveal a greater range in  $\delta^{18}\text{O}_{\text{SMOW}}$  values (+5.22 to +4.22 ‰) compared with comparable previous data from Day *et al.* (2014) for South African olivine melilitites from the Western Cape and Bushmanland (+4.99 to +5.26‰). These latter data have an average value of  $+5.14 \pm 0.17$  ‰, which is very close to the typical mantle olivine  $\delta^{18}\text{O}$  range of  $+5.18 \pm 0.28$  ‰ (Mattey *et al.*, 1994). However, it is important to note that the only olivine phenocrysts from South African melilitites having  $\delta^{18}\text{O}$  values below this mantle olivine range are found in those pipes emplaced within the Koegel Fontein intrusive complex, and only in a subset of these (Figure 54).

The Koegel Fontein complex is notable for the fact that dykes associated with it and the hydrothermally altered country rocks hosting it extends to extremely light  $\delta^{18}\text{O}$  values, as low as  $-3.0 \pm 0.2$ ‰ (Curtis *et al.*, 2013). Additionally, breccia pipes associated with the dykes contain fine-grained breccias (apparently composed of mixtures of alkaline lamprophyre (bostonite), basalt and local country rock) with  $\delta^{18}\text{O}$  values as low as  $-5.2 \pm 0.2$ ‰ (Olianti and Harris, 2018). Such low  $\delta^{18}\text{O}$  values were explained as the result of hydrothermal alteration (at 250-500°C) of the local country rock by fluids with exceptionally light  $\delta^{18}\text{O}$  values (-7 to -11) most likely during the latest Neoproterozoic when meteoric waters would have been extremely light due to global glaciation in the Cryogenian (Olianti and Harris, 2018). If this is indeed the correct explanation for these anomalously light oxygen isotope compositions, it remains unclear why they appear to be restricted to the area of the Koegel Fontein complex.

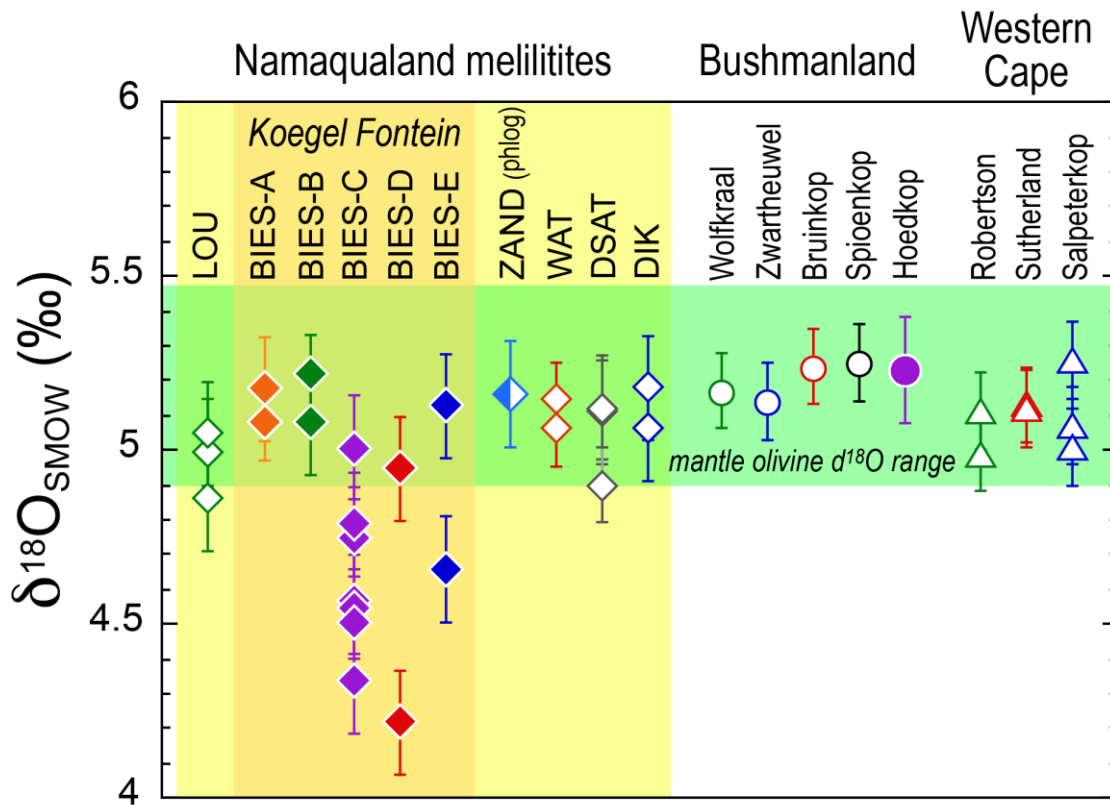


Figure 54. Oxygen isotope compositions of olivine phenocryst separates from South African melilitites from this study and Day *et al.* (2014). In Namaqualand (highlighted in yellow) and Bushmanland, the data are arranged by locality, from south to north, and the five melilitites pipes located within the Koegel Fontein complex (all from farm Biesiesfontein) are indicated. Also shown are data for the Western Cape melilitite localities (these and data for Bushmanland melilitites are from Day *et al.*, 2014). The oxygen isotope composition for the Zandkopsdrift (ZAND) melilitite was determined on phlogopite rather than olivine (data from Ogungbuyi *et al.* 2022). The green horizontal band represents the  $5.18 \pm 0.28\text{‰}$  range for mantle olivine determined by Matthey *et al.* (1994).

Given that (i) the olivines analysed are fresh and unaltered and (ii) there is no evidence that the olivines are xenocrystic in origin (i.e., derived from crustal or mantle xenoliths, since they tend to be at least reasonably close to Fe/Mg equilibrium with their hosts), the most plausible explanations for the oxygen isotope variations describe above are that the magmas parental to the Namaqualand melilitites assimilated a low- $\delta^{18}\text{O}$  component derived from the crust or mantle lithosphere beneath the Koegel Fontein complex. These two possibilities are evaluated below.

**Lithospheric mantle origin:** relatively low-MgO cores of olivines from southern African kimberlites, likely belonging to the Cr-poor megacryst suite, have been reported to extend from normal mantle compositions to low  $\delta^{18}\text{O}$  values (as low as  $+3.5\text{‰}$ ; Giuliani *et al.*, 2019; Xu *et al.*, 2021). These have been interpreted to result from the assimilation of lithospheric mantle heterogeneities with distinct oxygen isotope characteristics either due to metasomatic processes or to an origin as subducted oceanic crustal material (e.g., eclogite; Xu *et al.*, 2021). Such low  $\delta^{18}\text{O}$  lithospheric mantle materials could also potentially explain the light oxygen isotope compositions of olivines from some Namaqualand melilitites. However, two facts seem to argue against this hypothesis: (1) the  $\delta^{18}\text{O}$  values for the Namaqualand melilitite olivines that fall resolvably below the

5.18 ± 0.28 ‰ range in olivines from South African melilitites are limited to the pipes emplaced within the Koegel Fontein complex and (2) the anomalously low  $\delta^{18}\text{O}$  values in kimberlitic olivines have only been reported in Archaean cratonic settings, whereas the South African melilitites are all from Proterozoic or younger off-craton regions. There is no *a priori* reason why low  $\delta^{18}\text{O}$  heterogeneities in the lithospheric mantle should be localised beneath the Koegel Fontein complex, particularly since the low  $\delta^{18}\text{O}$  values here appear to be associated primarily with the local crustal country rock, not with the Koegel Fontein magmas, which likely originated in the mantle (Curtis *et al.*, 2013). The location of the Namaqualand melilitites in the mid-Proterozoic Namaqua-Natal province, therefore, makes a lithospheric mantle origin for the low  $\delta^{18}\text{O}$  values seem less likely.

**Crustal origin:** The light oxygen isotope compositions of hydrothermally altered country rock immediately surrounding the Koegel Fontein complex, and of igneous rocks apparently heavily contaminated by this country rock (Curtis *et al.*, 2013; Olianti and Harris, 2018). Additionally, the restriction of these anomalous low  $\delta^{18}\text{O}$  values to only the olivines from the Biesiesfontein melilitites emplaced in this same area, all strongly support the hypothesis that assimilation of local, middle or upper crust by the Biesiesfontein melilitites is responsible for the low  $\delta^{18}\text{O}$  values reported for olivines from these pipes. Below, a simple model is formulated to show the relationship between the assimilated oxygen isotope composition and the amount of assimilation that could explain the lowest  $\delta^{18}\text{O}$  values reported for the Biesiesfontein melilitite olivines.

It should be noted that there is no statistically significant difference in Pb isotope composition between the BIES pipes, which fall inside the Koegelfontein complex and have anomalously low  $\delta^{18}\text{O}$  and the remainder of the Namaqualand pipes. If anything, the BIES pipes have slightly more radiogenic age corrected  $^{206}\text{Pb}/^{204}\text{Pb}$  values with lower  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  for a given  $^{206}\text{Pb}/^{204}\text{Pb}$  (though not distinct outside of 1s uncertainties), which is the opposite of the expected effect of continental crustal addition.

## 7.2.2 ***Relationship between amount of crustal assimilation and assimilated composition constrained by oxygen isotopes.***

A simple mixing model (Figure 55) was created to constrain the percentage of assimilation required to lower the  $\delta^{18}\text{O}$  of the magma from an assumed normal mantle composition to that measured in most Biesiesfontein olivines with the lowest  $\delta^{18}\text{O}$  values. This model used a range in assimilated oxygen isotope compositions (with  $\delta^{18}\text{O}$  values from 1‰ down to -15 ‰) to generate a magma that could crystallize olivine with a  $\delta^{18}\text{O}$  as low as ~ 4.2 ‰ (i.e., the minimum  $\delta^{18}\text{O}$  value obtained from the lowest Namaqualand melilitite olivines).

This model assumes that the initial mantle-derived magma had a  $\delta^{18}\text{O}$  composition of +5.2 ‰. The model also assumes that the magma would crystallize minerals with the same  $\delta^{18}\text{O}$  values as itself, i.e., that the fractionation of oxygen isotopes between magma and crystals during the

crystallization of olivine was negligible (Zhao and Zheng, 2003). The model also assumes that the proportion of oxygen in the initial magma is essentially equal to that in the contaminant. The following formula applies:

$$X_{\text{assim}} * \delta^{18}\text{O}_{\text{assimilant}} + (1-X_{\text{assim}}) * \delta^{18}\text{O}_{\text{initial magma}} = \delta^{18}\text{O}_{\text{resulting magma}} \quad (3)$$

where:

- $X_{\text{assim}}$  is the proportion of assimilated material (a fractional value between 0 and 1, shown on plot for values between 0 and 0.25),
- $\delta^{18}\text{O}$  of the assimilant, on the plot this ranges between -15‰ and +1‰
- $X_{\text{assim}}$  (in %) is calculated for different values of  $\delta^{18}\text{O}$ , at intervals of 1‰ from -15‰ to +1‰
- $\delta^{18}\text{O}$  of the initial magma = +5.2 ‰
- $\delta^{18}\text{O}$  of the resulting magma is +4.2 ‰

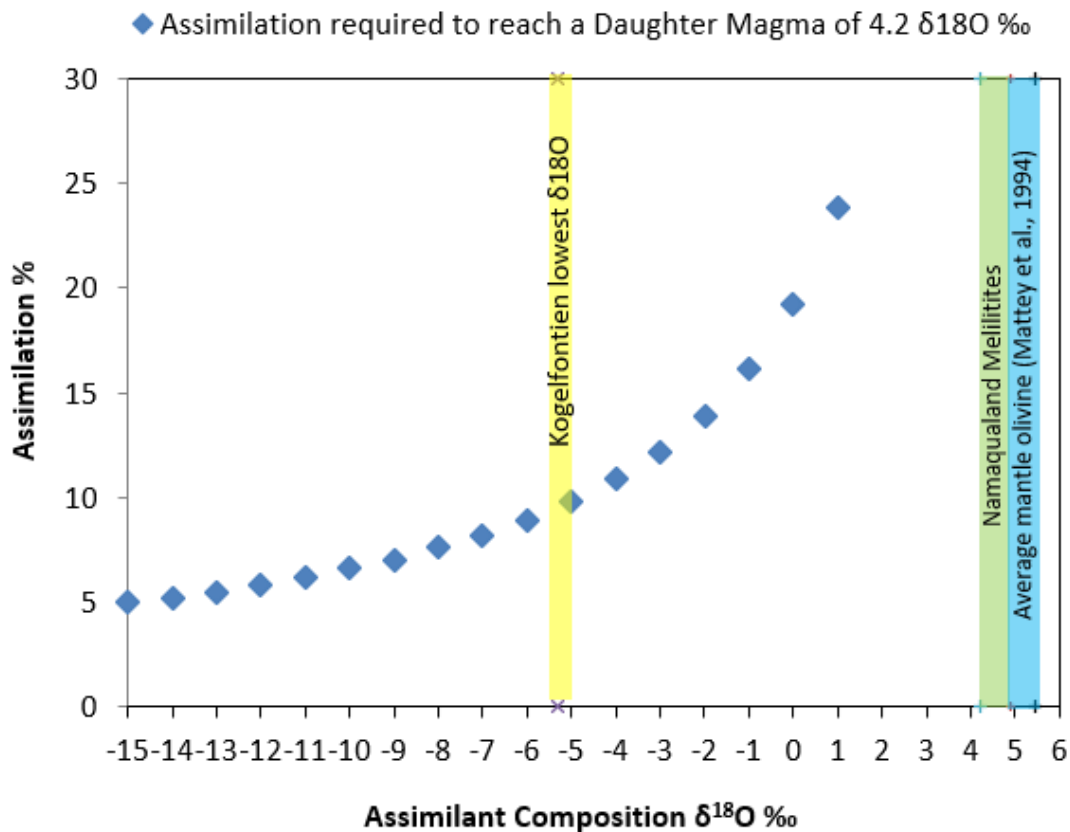


**Figure 55: Modelling curve for a scenario involving an initial magma with 5.2 ‰  $\delta^{18}\text{O}$  which assimilates a variable percentage (between 6 and ~24%) of an assimilant with a variable  $\delta^{18}\text{O}$  composition (between -15 and 1 ‰) resulting in a daughter magma with 4.2 ‰  $\delta^{18}\text{O}$ .**

The results indicate that if the assimilant had a  $\delta^{18}\text{O}$  value identical to that of the lightest  $\delta^{18}\text{O}$  fluid estimated by Olianti and Harris (2018) to have possibly been in equilibrium with the Koegel Fontein breccias ( -11 ‰), only 6.2% assimilation is required to produce a magma with a  $\delta^{18}\text{O}$  of +4.2 ‰ (Figure 55). Assimilants with oxygen isotope compositions equivalent to the lowest  $\delta^{18}\text{O}$  values

reported for Koegelfontein rocks (-5.3‰ to -4‰, Olianti and Harris, 2018) would require proportions of assimilation that are somewhat higher, of 9.5% to 11%, to explain the lowest  $\delta^{18}\text{O}$  Biesiesfontein olivines. Given that country rock and roof pendant gneiss from Koegel Fontein extend to  $\text{SiO}_2$  values as low as 63 wt.% (Curtis, 2009), such small amounts of assimilation cannot be excluded by elemental mixing models, therefore, are possible (Figure 59).

In contrast, assimilants such as average Koegel Fontein country rock gneiss (+4‰, Curtis *et al.*, 2013) requires 80% assimilation, which is clearly impossible to reconcile with the low  $\text{SiO}_2$  contents (and low Pb/Ce ratios) of Biesiesfontein melilitites and are therefore implausible.

On the basis of the above, it seems likely that the anomalously light oxygen isotope values reported for Biesiesfontein melilitites can be explained by approximately 10% assimilation (or less) of a crustal contaminant with extremely light oxygen isotope composition similar to the lowest  $\delta^{18}\text{O}$  values reported for the Koegel Fontein complex, as significantly higher proportions of local crust would result in detectably elevated  $\text{SiO}_2$  contents and Pb/Ce ratios. Further characterization of the Koegel Fontein country rocks may allow this estimate to be further refined. If this amount of assimilation did take place during the transit and emplacement of the Namaqualand melilitite magmas, there is no reason to expect that such assimilation did not also occur in the other Namaqualand melilitite pipes. It is likely only detectable in the Koegelfontein area because of the anomalously light oxygen isotope compositions of the local crust.

### **7.2.3 Major and trace element constraints on crustal assimilation in the Namaqualand melilitites:**

Primitive mantle-normalised incompatible element patterns for nearly all Namaqualand melilitite clusters show distinct negative K and Pb anomalies (as does the average composition, see Figure 56 below) whereas local upper crustal and lower crustal rocks from the region (this study and Schmitz *et al.*, 2004; Figure 56) show distinct positive Pb anomalies. This includes Proterozoic Namaqualand gneisses (pattern labelled NMC-UC) and igneous rocks from the mid-Cretaceous Koegelfontein complex (pattern labelled K-UC in Figure 56). These crustal rocks also often show negative anomalies for the HFSE (especially Nb and Ti, and sometimes Zr and Hf) which are not seen in the Namaqualand melilitites. These differences seem to argue against the occurrence of extensive crustal assimilation by the Namaqualand melilitites. The primitive mantle normalized trace element patterns for average global upper and lower continental crust from Rudnick *et al.* (2003) are also provided in Figure 56 (the middle crust is not shown as its pattern is very similar to the global upper crust). These patterns show significant similarities to the upper and lower continental crust (Table 16) from the study area, but little similarity to the patterns for the Namaqualand melilitites.

**Table 16. Continental crustal elemental compositions are used in this chapter.**

| Element                              | SAMLC<br>(1) | NMC-UC<br>(2) | K-UC<br>(2) | Upper C.<br>crust (3) | Lower C.<br>crust (3) |
|--------------------------------------|--------------|---------------|-------------|-----------------------|-----------------------|
| SiO <sub>2</sub> (wt.%)              | 49.74        | 73.93         | 75.22       | 66.6                  | 53.4                  |
| TiO <sub>2</sub> (wt.%)              | 0.99         | 0.26          | 0.19        | 0.64                  | 0.82                  |
| K <sub>2</sub> O (wt.%)              | 0.66         | 5.14          | 6.12        | 2.8                   | 0.61                  |
| P <sub>2</sub> O <sub>5</sub> (wt.%) | 0.20         | 0.09          | 0.01        | 0.15                  | 0.10                  |
| Rb (ppm)                             | 62           | 140           | 213         | 84                    | 11                    |
| Sr (ppm)                             | 560          | 50.0          | 17.4        | 320                   | 348                   |
| Y (ppm)                              | 18.5         | 13.6          | 40.6        | 21                    | 16                    |
| Zr (ppm)                             | 35.1         | 175           | 197         | 193                   | 68                    |
| Nb (ppm)                             | 4.75         | 6.57          | 34.5        | 12                    | 5.0                   |
| Ba (ppm)                             | 1874         | 375           | 173         | 628                   | 259                   |
| La (ppm)                             | 7.99         | 21.7          | 35.1        | 31                    | 8.0                   |
| Ce (ppm)                             | 21.6         | 44.1          | 86.6        | 63                    | 20                    |
| Nd (ppm)                             | 13.2         | 20.0          | 33.9        | 27                    | 11                    |
| Sm (ppm)                             | 3.25         | 4.08          | 6.99        | 4.7                   | 2.8                   |
| Eu (ppm)                             | 1.15         | 0.65          | 0.44        | 1                     | 1.1                   |
| Tb (ppm)                             | 0.51         | 0.53          | 1.16        | 0.7                   | 0.48                  |
| Dy (ppm)                             | 3.11         | 3.04          | 7.13        | 3.9                   | 3.1                   |
| Yb (ppm)                             | 1.94         | 1.44          | 4.82        | 1.96                  | 1.5                   |
| Lu (ppm)                             | 0.30         | 0.22          | 0.72        | 0.31                  | 0.25                  |
| Hf (ppm)                             | 0.89         | 5.73          | 6.80        | 5.3                   | 1.9                   |
| Pb (ppm)                             | 5.21         | 26.5          | 27.2        | 17                    | 4                     |
| Th (ppm)                             | 0.54         | 10.8          | 10.3        | 10.5                  | 1.2                   |
| U (ppm)                              | 0.73         | 1.36          | 3.71        | 2.7                   | 0.2                   |

Abbreviations are as follows: SAMLC, southern African mafic lower crust; NMC-UC, Namaqualand metamorphic complex upper crust; K-UC, Koegel Fontein upper crust; Upper C. crust, global average upper continental crust; Lower C. crust, global average lower continental crust. Sources of data are as follows: (1) Schmitz *et al.* (2004), (2), this study, (3) Rudnick *et al.* (2003).

Further evidence from Figure 57 reveals a lack of extensive crustal assimilation during the emplacement of the Namaqualand melilitites as there is no clear relationship between the chondrite-normalized REE patterns for Namaqualand melilitites and the chondrite-normalized REE patterns for the upper, middle and lower continental crust (Rudnick *et al.*, 2003) as well as the SAMLC (Schmitz *et al.*, 2004). The melilitites have quite uniform REE contents and nearly parallel REE patterns. The upper crustal samples collected from the vicinity of the pipes (both the Namaqualand upper crust (NMC-UC) and Koegelfontein upper crust (K-UC)) all show negative Eu anomalies which are not seen in the patterns for the Namaqualand melilitites. Local and regional lower and upper continental

crusts both often also show small positive or negative Ce anomalies, which are also not present in the Namaqualand melilitites.

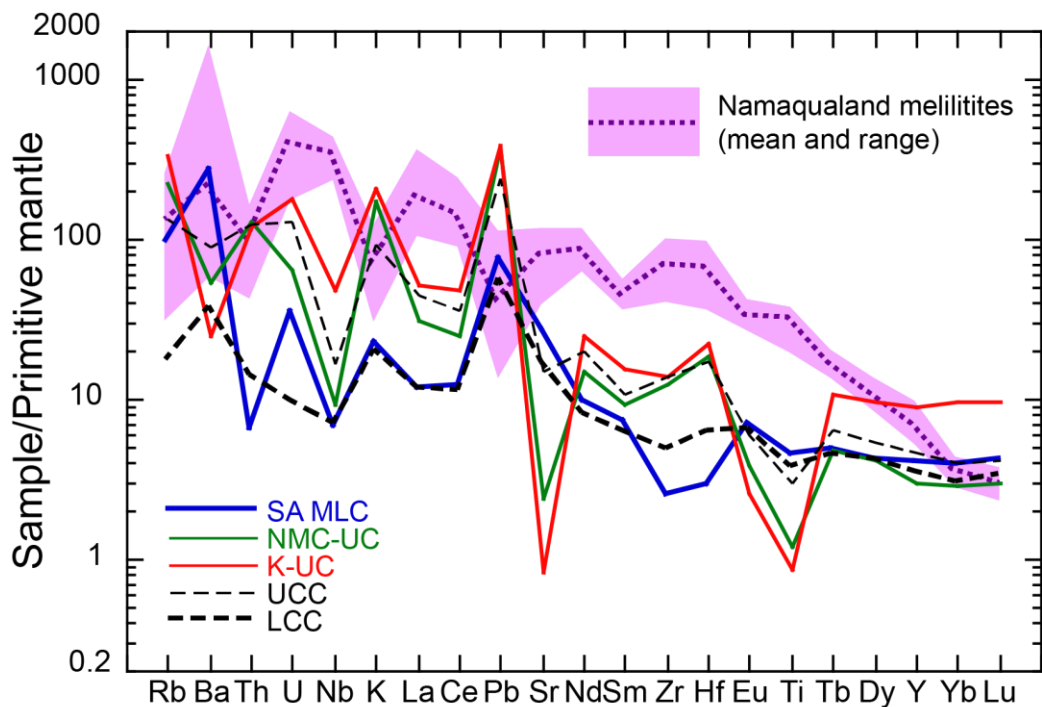


**Figure 56. Comparison of the primitive mantle normalized trace element patterns for the mean and range of the Namaqualand melilitites as well as regional and global continental crust compositions. SA MLC is off-craton South African mafic lower crust from Schmitz *et al.* (2004), NMC-UC and K-UC are Namaqualand metamorphic complex upper crust and Koegelfontein upper crust compositions from country rock samples obtained in this study and global upper (UCC) and lower (LCC) continental crust compositions from Rudnick *et al.* (2003). The Namaqualand melilitites lack the positive Pb anomalies (indeed, they typically show negative Pb anomalies) and negative Nb and Ti anomalies characteristic of the continental crust compositions plotted, therefore, shows no obvious indications of assimilation of continental crust.**

Mixing curves were calculated (shown plotted in Figure 58) to put constraints on the possible extent of crustal assimilation in the Namaqualand melilitites. One end-member was melilitite sample BIESE-1 which was selected because of its low Pb/Ce ratio and low SiO<sub>2</sub> content, making it a reasonable candidate for the sample with the lowest degree of crustal assimilation. Mixtures of this end-member with four different crustal compositions, (1) SAMLC (the average composition of mafic off-craton lower crustal granulite xenolith compositions from Schmitz *et al.* (2004), 2. LCC (lower continental crust from Rudnick *et al.* (2003)), 3. KUC, Koegelfontein upper crust and 4. NMC-UC, Namaqualand metamorphic complex upper crust (both the latter from this study) were calculated and plotted in Figure 58 with tick marks to show the proportion of end-member components. These mixing curves show the possible effects of bulk mixing between Namaqualand melilitite magma and the local crust. As mentioned above, the continental crust has high contents of both Pb and SiO<sub>2</sub>, whereas both of these are present at relatively low concentrations in the melilitites, particularly when compared to other incompatible elements.

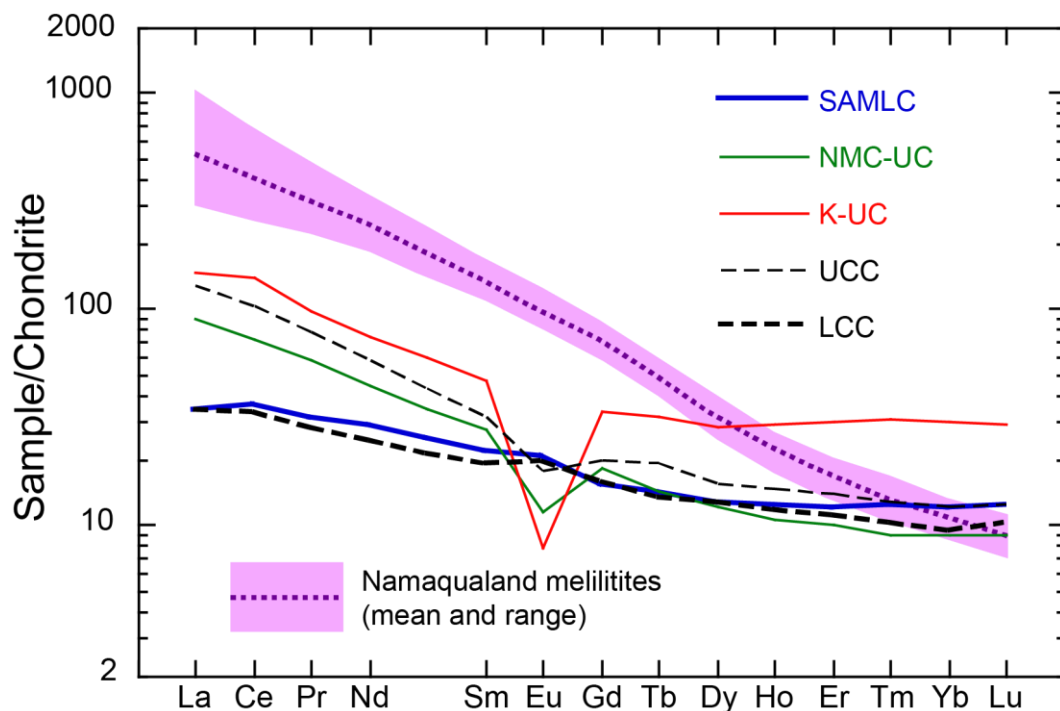


**Figure 57. Chondrite normalized REE patterns for the Namaqualand melilitites (average and range) and also the composition of regional and global continental crust compositions. Abbreviations are the same as in Figure 3. No indications of crustal assimilation in the melilitites are apparent.**

Figure 58 shows the Namaqualand and Bushmanland melilitites on plots of (a)  $\text{SiO}_2$  vs  $\text{Pb/Ce}$  and (b)  $\text{Pb/U}$  versus  $\text{Pb/Ce}$ . The plots in Figure 58 indicate that virtually all of the Namaqualand melilitites fall at  $\text{Pb/Ce}$  ratios above all of the mixing curves on both plots, likely reflecting that the variation of  $\text{Pb}$  in these rocks is not due to the variable addition of continental crust. Even for the loosest interpretation, there is no way that the Namaqualand melilitites could represent mixtures with more than 10-20% crust of any composition and, interestingly, these plots show even less potential for crustal assimilation in the Namaqualand melilitites compared to the neighbouring Bushmanland melilitites, which have higher average  $\text{SiO}_2$ ,  $\text{Pb/Ce}$  and  $\text{Pb/U}$  ratios.

These plots also fail to support significant assimilation of continental crust as a cause of compositional variation of the Namaqualand and Bushmanland melilitites. It is possible that an assimilation-fractional crystallization (AFC) process could be responsible for the Namaqualand melilitites falling off the mixing curves in Figure 58-a since olivine crystallization would drive the magma composition toward lower  $\text{SiO}_2$  values, but this does not offer an explanation of why the Namaqualand melilitites fall off the mixing curves in Figure 58-b, which would not be significantly affected by crystallization of olivine or other major phases (e.g., clinopyroxene, melilite, magnetite, phlogopite; e.g., Onuma *et al.*, 1981; Lundstrom *et al.*, 2006; Adam *et al.*, 1993).

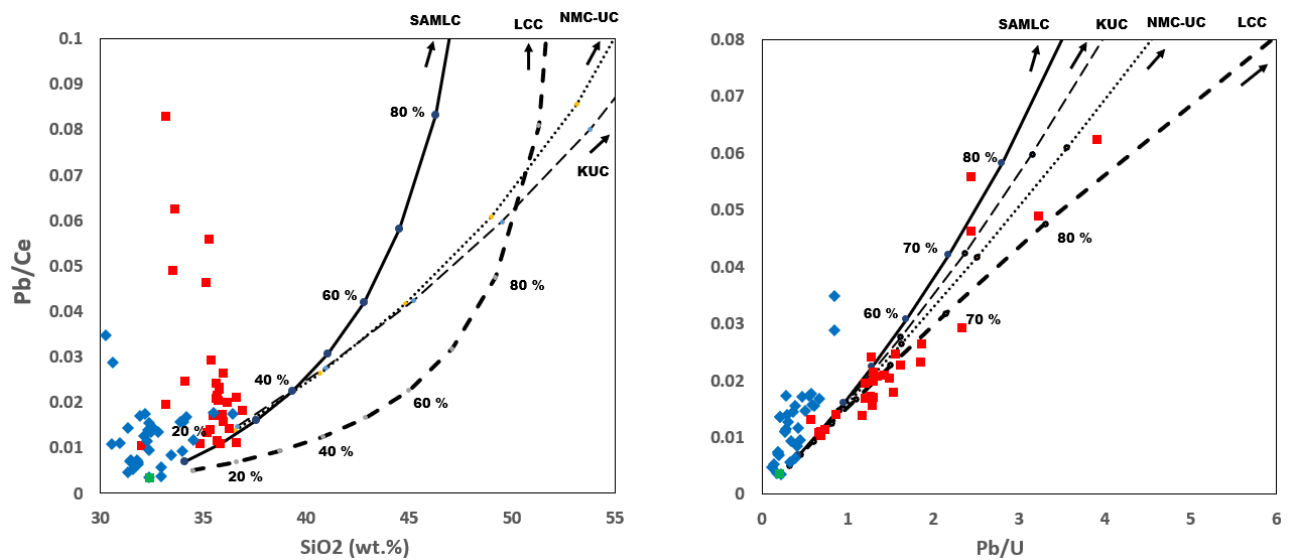


Figure 58: (a) wt.% SiO<sub>2</sub> and (b) Pb/U, both plotted versus Pb/Ce ratios for Namaqualand (blue diamonds) and Bushmanland melilitites (red squares). Bushmanland data are from Janney *et al.* (2017). Also shown are mixing curves between sample BIESE-1 (indicated by green square), a Namaqualand melilitite with among the lowest Pb concentrations and Pb/Ce and Pb/U ratios of all Namaqualand melilitites, and various upper and lower crustal compositions: LCC (lower continental crust estimate of Rudnick *et al.*, 2003), SAMLC (mean mafic granulite xenolith compositions from the Markt (off craton) kimberlite, Northern Cape, South Africa, from Schmitz *et al.*, 2004), NMC-UC (upper crust from the Namaqualand Metamorphic complex, representing an average of country rock samples LOU-CR1, DIK-CR1 and DSAT-CR1), and KUC (upper crust from the Koegelfontein complex, representing the average composition of samples RTPT-1 and BIESD-CR1). Note that, in both diagrams, the Namaqualand melilitites tend to show compositions consistent with lower degrees of continental crustal assimilation than the near-primary Bushmanland melilitites.

#### 7.2.4 *Pb and Hf isotopic constraints on crustal assimilation in the Namaqualand melilitites:*

The metamorphic and igneous rocks composing the upper continental crust of Namaqualand and Bushmanland are characterised by relatively radiogenic <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb ratios for a given <sup>206</sup>Pb/<sup>204</sup>Pb values (Figure 59; Reid *et al.*, 1997; Curtis *et al.*, 2011), with the Koegelfontein igneous rocks having a Pb isotope compositions transitional between Bushmanland gneisses and mantle-derived rocks, such as MORB and kimberlites. In contrast, lower crustal granulite xenoliths from off-craton kimberlites in western South Africa have unradiogenic <sup>206</sup>Pb/<sup>204</sup>Pb, <sup>207</sup>Pb/<sup>204</sup>Pb and <sup>208</sup>Pb/<sup>204</sup>Pb ratios falling well below those of most upper crustal rocks as well as nearly all mantle-derived rocks, only barely overlapping with the low <sup>206</sup>Pb/<sup>204</sup>Pb edge of the MORB field (Huang *et al.*, 1995). It is clear from Figure 59 that the Namaqualand melilitites are well within the range of values for mantle-derived magmas, such as HIMU, OIB, MORB and southern African kimberlites, and are no closer to the values for regional upper crustal basement or lower crust than the near-primary Bushmanland melilitites or Warmbad kimberlites. Fractional crystallization and assimilation are often correlated as part of an AFC process in igneous rocks (e.g., DePaolo, 1981), and, given the relatively high Pb contents of continental crust and the relatively distinct Pb isotopic composition of most crustal

and mantle-derived rocks in southern Africa, Pb isotopes should be a sensitive tracer of crustal assimilation. However, the lack of difference in Pb isotope composition between the Namaqualand and Bushmanland melilitites, except in that the former extend toward more extreme HIMU OIB-type compositions very unlike typical continental crust, would seem to argue against significant assimilation of continental crust by the Namaqualand melilitites.

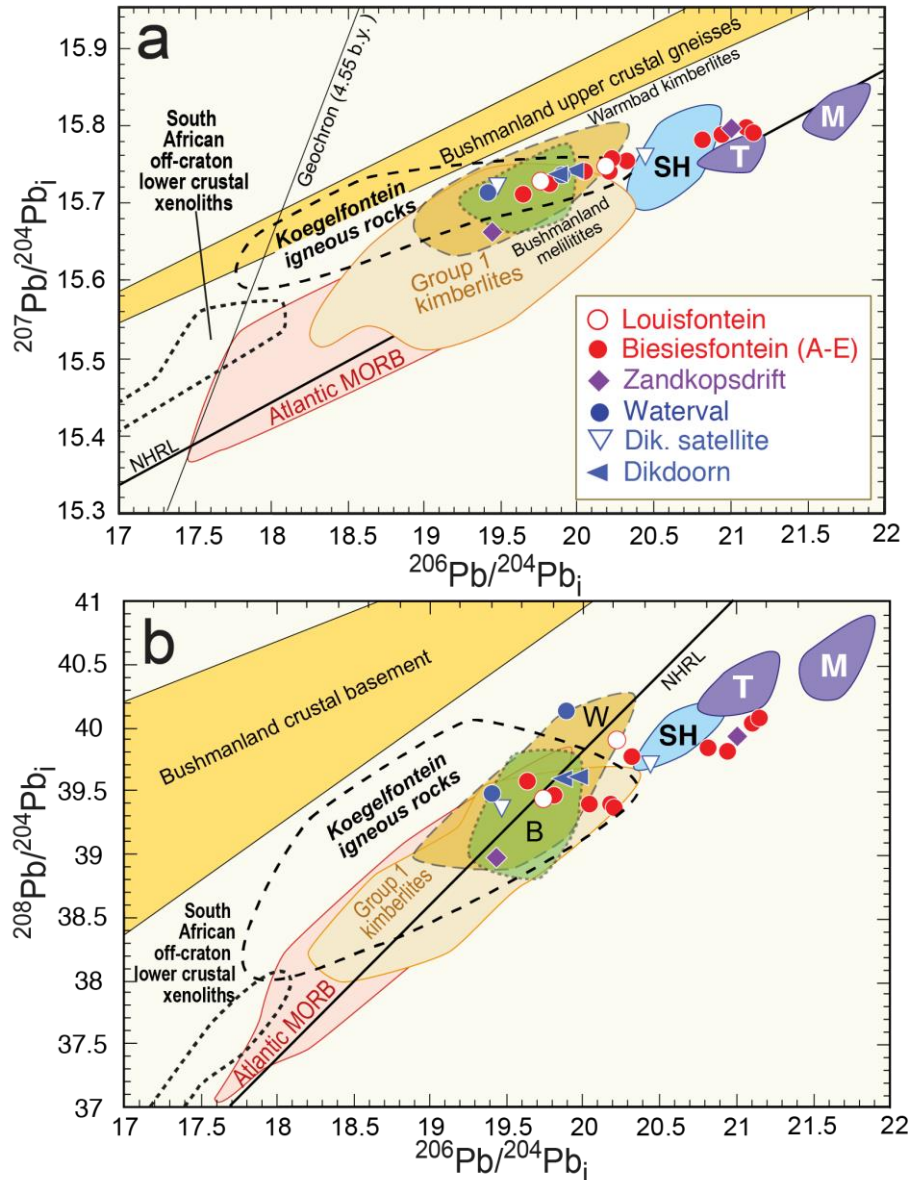


**Figure 59.** Plots of initial Pb isotope composition of the Namaqualand melilitites (a)  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{207}\text{Pb}/^{204}\text{Pb}$ , (b)  $^{206}\text{Pb}/^{204}\text{Pb}$  versus  $^{208}\text{Pb}/^{204}\text{Pb}$ . Also shown are fields for the Bushmanland melilitites and Warmbad kimberlites (Janney *et al.*, 2017), Atlantic MORB (PETDB, 2018), southern African kimberlites (Group 1.; Smith, 1983; Davies *et al.*, 2001; Collerson *et al.*, 2010) and HIMU-type ocean island basalts (GeoROC database, 2018), as well as Bushmanland whole rock gneisses (Reid *et al.*, 1997), igneous rocks from the Koegelfontein Igneous Complex (Curtis *et al.*, 2011) and whole-rock lower crustal granulite xenoliths from off-craton kimberlites in western South Africa (Huang *et al.*, 1995). For these crustal rocks, only a subset has Pb, Th and U concentration data so present-day Pb isotope compositions are plotted. However, corrections for radiogenic growth to the age of the Namaqualand melilitites ( $\approx 50$  Ma) for these rocks are likely to be small due to the relatively low U/Pb and Th/Pb elemental ratios of most of these samples (typically less than 1 and 2, respectively). Abbreviations: B, Bushmanland melilitites, SH, St. Helena, M, Mangaia, T, Tubuai and W, Warmbad kimberlites. NHRL indicates the Northern Hemisphere Reference Line of Hart (1984).

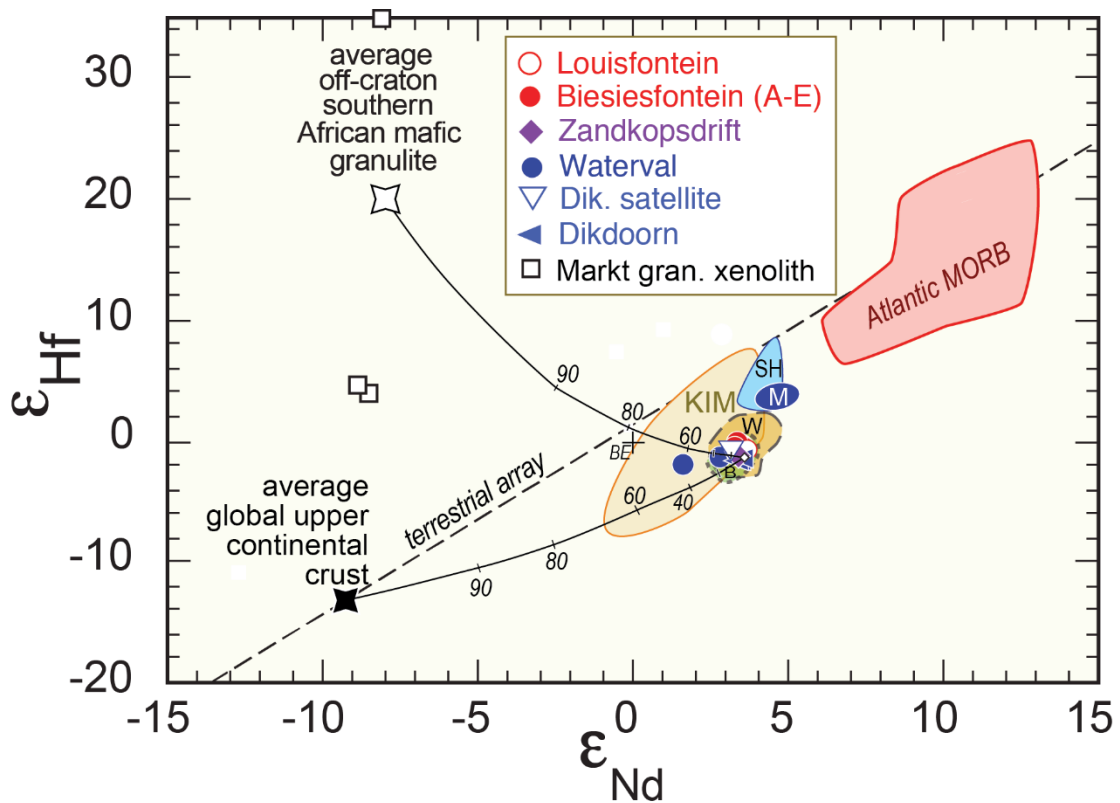


**Figure 60:** Plot showing Nd-Hf isotope data for the Namaqualand melilitites as well as fields for the Bushmanland melilitites and Warmbad kimberlites (Janney *et al.*, 2017), other southern African kimberlites (Group 1 only, Nowell *et al.*, 2004), HIMU-type ocean island basalts from St. Helena and Mangaia (GeoROC database, 2018), and Atlantic MORB (PETDB, 2018). Also shown are whole-rock Nd-Hf isotope data for granulite lower crustal xenoliths from the off-craton Markt kimberlite (Schmitz *et al.*, 2004), and mixing curve between sample DIK-12 and the average granulite composition, and between DIK-12 and the average global upper crustal composition (Chauvel *et al.* 2014) with proportions crust in percent. Abbreviations are as follows: B, Bushmanland melilitites, KIM, southern African kimberlites (Group 1), M, Mangaia OIB, S, St. Helena OIB, W, Warmbad kimberlites.

Because of the geochemical similarity of the Sm/Nd and Lu/Hf isotope systems, most crustal and mantle-derived rocks tend to lie close to a single regression line on plots of  $\epsilon_{\text{Nd}}$  versus  $\epsilon_{\text{Hf}}$  that has been termed the 'terrestrial array'. Rocks can sometimes fall far above or below this line if their Sm/Nd and Lu/Hf ratios become decoupled due to processes such as preferential retention or loss of the mineral zircon (which has extremely high Hf/Nd ratios; Vervoort *et al.*, 2011), or due to ancient melting involving garnet-bearing lithologies (garnet strongly retains Lu over Hf during partial melting). This change may also be driven by progressive mantle metasomatism (e.g. Fitzpayne *et al.*, 2019) where the fractionation of Lu from Hf occurs due to the Influence of kimberlite melts.

Janney *et al.* (2017) found that the Namaqualand-Bushmanland melilitites have Nd-Hf isotope compositions that fall significantly below the terrestrial array, similar to southern African kimberlites. In contrast, off-craton lower crustal granulite xenoliths from western South Africa tend to fall significantly above the terrestrial array, likely due to them representing the garnet-bearing residues of ancient partial melting (Schmitz *et al.*, 2004). This contrasts with the average composition of the global upper continental crust, which lies on the terrestrial array (Chauvel *et al.*, 2014). Because of their distinct compositions, Nd-Hf isotope ratios provide another means to detect the mixing of lower

or upper crust into the Namaqualand melilitites. However, due to the relatively low  $\epsilon_{\text{Nd}}$  and  $\epsilon_{\text{Hf}}$  concentrations of the average global upper crustal composition and the close clustering of the Namaqualand melilitites there is less evidence of a trend in the Namaqualand melilitites to indicate crustal contamination when compared to the trends observed in the Pb isotope data. This is similar to the average off-craton southern African mafic granulite where the data presented does not show a clear trend along the mixing curves to support the assimilation of this material. This indicates that Nd and Hf isotopes are less sensitive tracers to contamination compared to the Pb isotopes.

The Namaqualand and Bushmanland melilitites and most Warmbad kimberlites plot in a restricted field that lies 6 to 9  $\epsilon_{\text{Hf}}$  units below the terrestrial array in a plot of  $\epsilon_{\text{Nd}}$  versus  $\epsilon_{\text{Hf}}$  (Figure 60), overlapping with the field for southern African kimberlites. They do not show any significant variation consistent with mixing with crustal material with the exception of samples from the locality Waterval (WAT), which extends to significantly lower  $\epsilon_{\text{Nd}}$  and slightly lower  $\epsilon_{\text{Hf}}$  values, as well as slightly higher  $^{208}\text{Pb}/^{204}\text{Pb}$  for a given  $^{206}\text{Pb}/^{204}\text{Pb}$  value compared to the other Namaqualand melilitites. However, the melilitites from this locality are by far the most primitive and least fractionated of the Namaqualand cluster (with Mg# values of 70-71) and their distinct isotopic compositions compared to the other melilitites, combined with their strong negative Pb anomalies on primitive mantle-normalised diagrams (which is inconsistent with significant crustal assimilation), appear to be most likely due to a more enriched mantle source relative to the other melilitites, rather than a greater degree of crustal assimilation in their petrogenesis.

### **7.3. Source mineralogy and conditions of melting for the Namaqualand melilitites:**

Olivine melilitites, ultramafic lamprophyres and archetypal (i.e., Group 1) kimberlites are considered to be the products of low degrees of partial melting of carbonated peridotite sources within the garnet stability field according to experimental and analytical studies (e.g., Brey *et al.*, 1978; Ringwood *et al.*, 1992; Kesson *et al.*, 1994; Wilson *et al.*, 1995; Lee and Wyllie, 1997; Tappe *et al.*, 2006). The source mineralogy and melting conditions of the Namaqualand melilitites may be estimated using trace element modelling, partition coefficients from the literature and reasonable assumptions of the modes and melt contributions of the major mantle minerals. The modelling of the source mineralogy and conditions of melting of the Namaqualand melilitite magmas using trace elements and trace element ratios is a useful approach because they do not require precise knowledge of the composition of the minerals involved, but only the appropriate mineral-melt distribution coefficients. In this section, trace elements will be used to model if the Namaqualand melilitites may be derived from a common mantle source.

### 7.3.1 *Constraints on the degree and depth of melt generation from the rare earth elements:*

Experimental work has shown that mildly carbonated, ultramafic melts similar to South African olivine melilitites can be formed by melting carbonated garnet lherzolite at pressures of 3.0-3.5 GPa (Brey, 1978). This depth range is well within the garnet stability field (experimentally determined to be  $\geq 2.5$  Ga or  $\geq 75$  km; Hirschmann and Stolper, 1996), but it is also true that (1) melting in many environments takes place over a range of pressures (Asimow and Longhi, 2004) and (2) the garnet-spinel transition is not necessarily sharp and mantle can be both spinel- and garnet-bearing over a significant depth interval if the mantle is moderately melt-depleted (i.e., has a significant ratio of Cr/Al; Klemme, 2004).

Qualitative constraints on the degrees of melting and depth of melt generation can be obtained using the REE because (1) they are a group of incompatible elements with the same valence state and smoothly varying ionic radius which controls their incompatibility during partial melting. Mantle peridotites typically do not vary greatly in their relative abundances of the middle and heavy REE, and (2) because garnet, which is present in peridotite only at pressures greater than 15Kbar (i.e., >60km) and garnet is the only common mantle mineral in which some REEs (the heavy REE) are compatible (O'Hara *et al.*, 1971). The modelling of partial melting processes based on the REE does require assuming a mantle lithology (e.g., peridotite versus eclogite or pyroxenite) and the REE composition of the mantle source. For partial melts of any given composition, the relative abundances of the middle REE are most affected by the degree of melting, while the middle to heavy REE is most affected by the amount of garnet present during melting, or in the case of polybaric melting, the amount of melting occurring in the presence of garnet (McKenzie and O'Nions, 1991), although these are also affected by the degree of melting (see melting grid in Figure 10 below). Melts generated from a mantle source with residual garnet will have lower HREE concentrations than melts generated from garnet-free sources with otherwise identical mineralogy.

Figure 61 shows a plot of chondrite-normalized Tb/Yb versus Sm/Tb ratios containing a grid of modelled melt compositions created by varying degrees of partial melting (from 0.1 to 10%) of a series of three different mantle sources which contain varying ratios of spinel to garnet. The source composition was modelled with modal proportions to include 45 % olivine, 25 % clinopyroxene and 10% orthopyroxene as well as 20% of garnet or spinel. This mineralogy was used to model a range in melts that covers the compositions of the Namaqualand olivine melilitites and the group 1 kimberlites. The three sources are labelled in Figure 61 as (1) **100% Spinel** (i.e., garnet-free peridotite); (2) **70% Spinel:30 % Garnet** and (3) **100% Garnet** (i.e., spinel-free peridotite). The composition with the proportion of spinel and garnet as 75% spinel and 25 % garnet is a mixture and is meant to simulate the average for melting near the garnet/spinel stability field boundary.

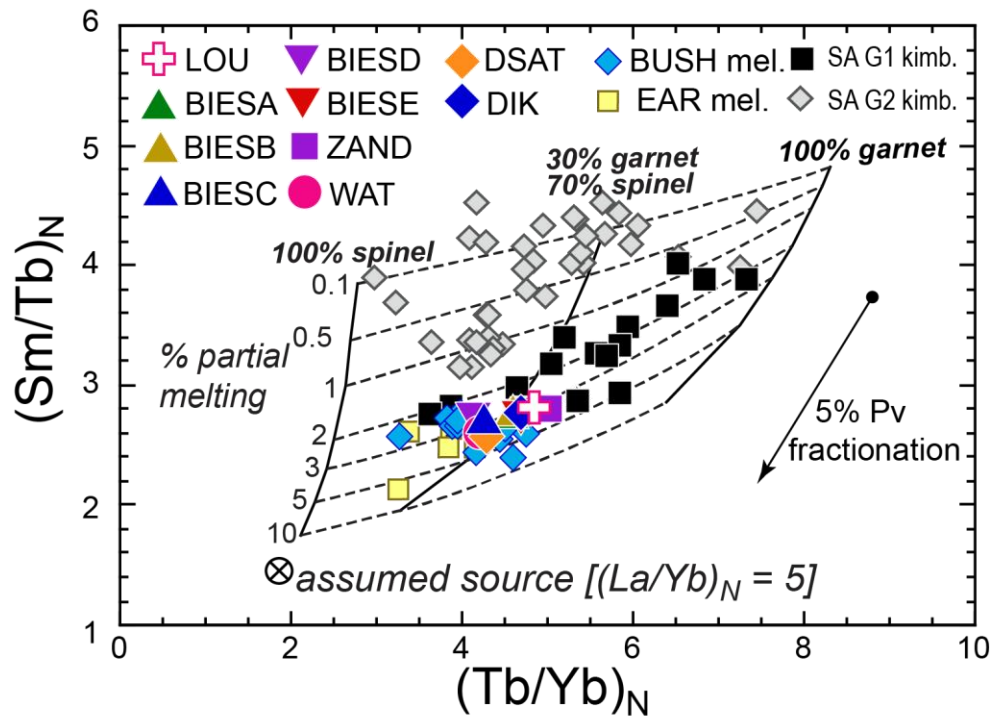


**Figure 61.** Chondrite-normalised Tb/Yb versus Sm/Tb ratios for the Namaqualand olivine melilitites (values averaged by locality) compared with similar data averages for the Bushmanland olivine melilitites as well as data for South African group 1 and group 2 kimberlites, also averaged by locality (le Roex *et al.*, 2003; Becker and le Roex, 2006) and olivine melilitites from the East Rift of the East African Rift System (Keller *et al.*, 2006). The melting grid shows compositions of melts of an assumed source composition calculated for different degrees of partial melting (0.1 to 10%) of a peridotite mantle source having variable relative proportions of spinel and garnet. The vector indicates the effect of 5% fractional crystallization of perovskite using the partition coefficients of Chakhmouradian *et al.* (2013). Assumed modal and melt contribution proportions of olivine/orthopyroxene/clinopyroxene/ (spinel + garnet) were 0.45/0.25/0.1/0.2 and 0.25/0.25/0.25/0.25. Partition coefficients used are given in Appendix Z.

Normalization was done using chondrite values from McDonough and Sun (1995). Note that Namaqualand and Bushmanland melilitites largely overlap and that they plot in a location intermediate between that of Group 1 kimberlites and rift melilitites. The melting grid and the modelled source are only included for purposes of comparison, they are not intended to represent actual estimates of melting conditions.

These compositions are assumed to be from a moderately enriched mantle source  $(La/Yb)_N=5$  with a linear REE pattern. The melting grid in Figure 61 provides a rough guide for the effects of the different degrees of partial melting at different ratios of garnet to spinel (which could be explained by different depths of melting) for the same moderately enriched mantle source.

The grid in Figure 61 shows that changes in the degree of partial melting of an assumed mantle source mainly cause variations in  $(Sm/Tb)_N$  ratios (although this will also have a smaller effect on Tb/Yb ratios), whereas changes in the ratio of spinel to garnet in the mantle source for a given degree of partial melting (i.e., a proxy for depth of partial melting) mainly affects the  $(Tb/Yb)_N$  ratio. The Namaqualand and Bushmanland melilitites fall within a restricted region overlapping with the lowest Sm/Tb and Tb/Yb ratios of Group 1 kimberlites and the highest Sm/Tb and Tb/Yb ratios of East African Rift melilitites suggesting intermediate degrees of melting and proportions of garnet in the melting residue. It is possible that fractionation of REE-bearing phases, such as perovskite, can affect these ratios (see perovskite fractionation vector in Figure 61) but the high degree of overlap between

the Namaqualand and Bushmanland melilitites strongly suggests that such fractionation has not had an important effect on Sm/Tb or Tb/Yb ratios.

It should be remembered that this kind of modelling can only be considered qualitative since variations in mantle source enrichment and modal mineralogy/lithology will also have a major effect on these two REE ratios, and indeed, such differences are likely more responsible for the higher (Sm/Tb)<sub>N</sub> values of Group 2 kimberlites (orangeites) relative to Group 1 kimberlites than a quantitative difference in the average degree of melting (Becker and le Roex, 2006). So while this analysis can say with some confidence that the Namaqualand (and Bushmanland) melilitites were generated at depths and degrees of melting intermediate between those of kimberlites and East African Rift-related olivine melilitites (making the assumption that their similarity in Nd isotope ratios indicates a similar REE composition of their sources), it is not possible to place more quantitative constraints on their depths degrees of melting without more detailed knowledge of the modal mineralogy and composition of their mantle sources.

### **7.3.2 *Trace element and constraints on the degree of melting and source mineralogy:***

A different and somewhat more quantitative modelling approach is to use a wider array of incompatible trace elements to forward model the source composition of the melilitites for a variety of plausible source mineralogies and melting conditions. Parallel modelling was undertaken of samples from the Waterval melilitite pipe in Namaqualand (the only one of this cluster that has a near-primary composition) and the Zwartheuwel and Hoedkop pipes in southern and northern Bushmanland, respectively, which have lesser and greater enrichments, respectively, in the most highly incompatible elements. The purpose of this modelling is to (1) determine what degrees of melting would result in the greatest agreement in the calculated source compositions of melilitites from each of the pipes. This is particularly important for the mildly to moderately incompatible elements (which are more affected by conditions of melting and less subject to variations caused by different degrees of source enrichment). (2) determine the effect on the source composition of including possible exotic residual minerals, such as phlogopite, in the source mineralogy, and (3) compare the relative abundances of highly incompatible elements (Nb to Rb) in the calculated source compositions to determine whether there appear to be significant variations in these elements that are correlated with location and other factors.

Average compositions for samples from each locality were used for the modelling to get the most representative compositions. Zwartheuwel and Hoedkop were selected from amongst all the Bushmanland melilitite localities because of their locations in southern and northern Bushmanland (to give the maximum geographic spread) and also because they lack significant positive anomalies in Ti, Zr and Hf in primitive mantle-normalised incompatible element patterns. These anomalies are

relatively common in Bushmanland melilitites and likely result from the accumulation of oxides during magma ascent.

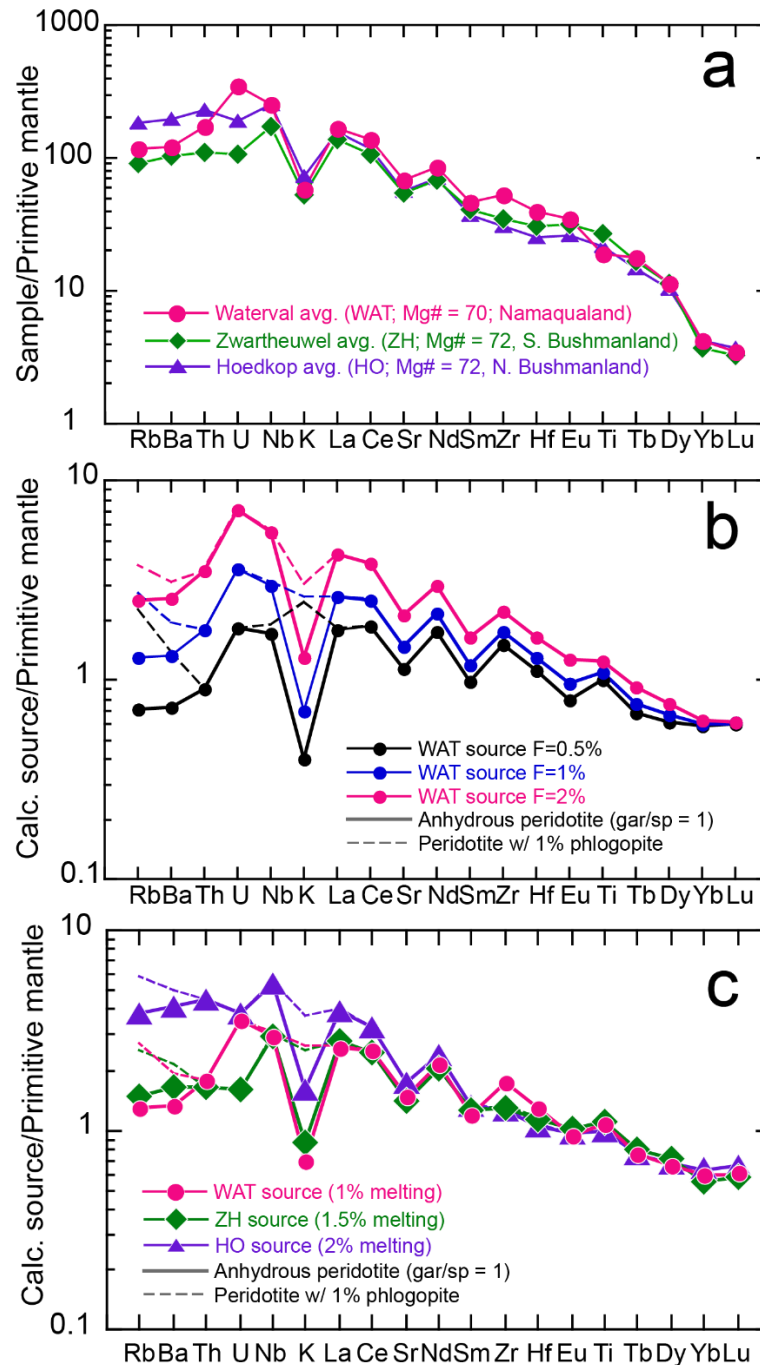


**Figure 62. (a) Primitive mantle (PM) normalised incompatible element diagram for the average olivine melilitite composition from Waterval (Namaqualand) as well as Zwartheuwel and Hoedkop in southern and northern Bushmanland, respectively. (b) PM normalised calculated source compositions for WAT melilitite assuming 0.5, 1.0 and 2.0% batch partial melting of both anhydrous and phlogopite-bearing peridotite, and (c) comparison of calculated PM normalised source compositions for WAT (assuming 1% melting), and ZH and HO melilitites (assuming 1.5% and 2% partial melting, respectively) for both anhydrous and phlogopite peridotite sources. Assumed modal and melt contribution fractions of olivine/orthopyroxene/ clinopyroxene/ (spinel + garnet) in peridotite are 0.63/0.23/0.1/0.04 and 0.2/0.2/0.44/0.16, respectively (D values for all minerals except phlogopite are from le Roex *et al.*, 2003 except for Th and U which are from McKenzie and O'Nions, 1991). Models including phlogopite have modal and melt contribution fractions of 0.01 and 0.1, respectively, with the other mineral proportions reduced proportionately (phlogopite D values for Rb, Ba and Nb are from Adam *et al.*, 1993, others are from LaTourrette *et al.*, 1995).**

In the modelling shown below (Figure 62), source compositions are calculated assuming a range of low degrees (0.5 to 2%) of batch partial melting of reasonable lherzolite source mineralogies (see figure caption for details). A 50:50 garnet spinel ratio is assumed for all sources because (1) it is relatively consistent with the REE modelling in Figure 61 above and (2) this gives similar HREE abundances for all calculated sources in Figure 62c below. In these models, higher degrees of melting result in higher calculated source incompatible element abundances because the source enrichment in incompatible elements must be greater as the extent of partial melting increases in order to generate the same melt composition.

Model source compositions were calculated for both an anhydrous garnet-spinel lherzolite mineralogy and for the same mineral assemblage that includes 1% phlogopite (see Figure 62 caption above for details). Rogers *et al.* (1992) interpreted that phlogopite was an important residual phase in the mantle source of Namaqualand melilitites on the basis of K/Nb and Rb/Sr ratio variations. The evidence for the involvement of phlogopite is discussed further below.

There are two key interpretations that can be drawn from the models in Figure 62. First, for the moderately to mildly incompatible elements (i.e., from Sr to Lu, with the possible exception of Zr) relatively uniform source compositions for the three pipes are calculated when using degrees of melting of 1% for Waterval (WAT), 1.5% for Zwartheuwel (ZH) and 2% for Hoedkop (HO). In other words, the abundances of all of these elements (again excepting Zr, which is slightly higher in WAT) calculated for the sources of these melilitites are nearly equal using these degrees of melting. The more highly incompatible elements show strong negative K anomalies and low abundances of Rb, Ba and Th relative to Nb. U is enriched relative to Th in the WAT source whereas its primitive mantle normalised abundance in ZH and HO is similar to that of Th.

Second, if 1% phlogopite is included in the source assemblage, the negative K anomalies in the primitive mantle-normalised source patterns largely or entirely disappear and all three patterns display a positive slope from Th to Rb. In the case of HO, this results in a nearly linear, negatively sloping PM-normalised pattern from Rb to Lu, whereas for WAT and ZH, the patterns are also negatively sloping but with significant relative depletions in the most incompatible elements (Rb, Ba, Th) and major increases in relative abundances between Th and U (WAT) or between U and Nb (ZH).

Based on this modelling alone, there is no clear reason to prefer the models with phlogopite versus those with anhydrous peridotite. However, there are large fractionations of trace element ratios, particularly Nb/Rb, that can only be explained by the involvement of phlogopite in the petrogenesis of the Namaqualand-Bushmanland melilitites. Figure 63 below shows variations of Nb/Rb versus Ba/Rb in the Namaqualand and Bushmanland melilitites and the Warmbad kimberlites. The latter two sample groups show moderate variations of Nb/Rb from near primitive mantle values ( $\approx 1$ ) to values of  $\approx 5$ , which correlate positively with Ba/Rb ratios. Such variations are consistent with variable degrees of partial melting of a mantle source containing a small amount ( $\approx 1\%$ ) of residual phlogopite. In contrast, the Namaqualand melilitites show much larger variations in Nb/Rb ratios (from 1 to 14) which also correlate positively with Ba/Rb ratios, but with a much shallower slope (Figure 63). Such large

variations in Nb/Rb could be due to a source with a large modal proportion of phlogopite (see the trajectory of melt compositions of a source containing 5% modal phlogopite), but the shallow linear array described by the Namaqualand melilitite data are not consistent with this. The least squares fractionation modelling shown in Table 15 indicates up to 10% total crystallization of phlogopite (i.e., total % crystallization modal proportion of phlogopite in fractionating assemblage) in some crystallization steps. Fractional crystallization of phlogopite can also cause large shifts in Nb/Rb ratios (see vectors in Figure 63 below). However, the fractionation vectors are shallower in slope (or have a shallow negative slope, depending on the source used for partition coefficients) than displayed by the Namaqualand melilitites. This strongly suggests that the Namaqualand data array in Figure 63 is due to a combination of partial melting of a phlogopite-bearing source and subsequent fractional crystallization of phlogopite. The Zandkopsdrift melilitites have anomalously high Ba/Rb ratios falling off the main Namaqualand trend, which is likely due to their unique association with carbonatite at this locality (which has very high Ba/Rb; Ogungbuyi *et al.*, 2022; Nelson *et al.*, 1988).

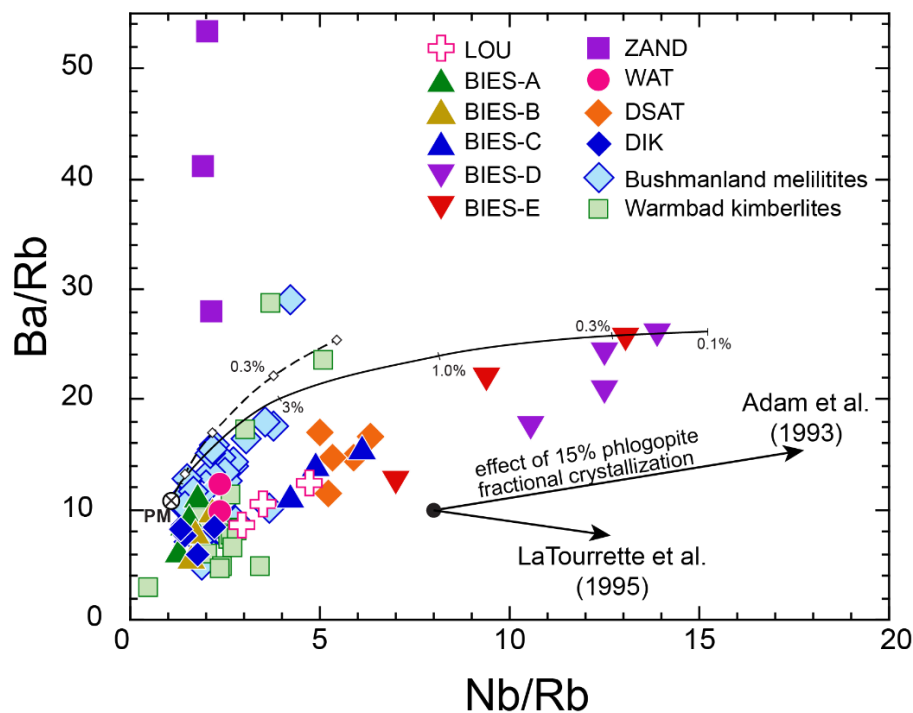


**Figure 63.** Nb/Rb versus Ba/Rb for Namaqualand and Bushmanland melilitites and Warmbad kimberlites (data for the latter two groups are from Janney *et al.*, 2017). Circle labelled "PM" indicates the primitive mantle composition of McDonough and Sun (1995). Curves show the composition of different degrees of melting of phlogopite-bearing peridotite. Melt compositions are calculated using the parameters in Figure 61, except that the curves have different phlogopite modal proportions and melt contributions (dashed shows the trajectory of melts of a source with 1%/10% phlog. modal and melt proportion and the solid line shows melts of a source with 5%/50% modal and melt proportion of phlogopite, all other mineral modes and melt contributions are in the same proportions as given in Figure 61). Also shown are vectors indicating the effect of fractional crystallization of 15% phlogopite, calculated using the D values of Adam *et al.* (1993) and LaTourrette *et al.* (1995). Note that the slope of the Namaqualand data is steeper than either of the fractionation vectors. The anomalously high Ba/Rb ratios for the Zandkopsdrift melilitites are likely related to the fact that they are associated with the Zandkopsdrift carbonatite, which (like nearly all carbonatites) also has extremely high Ba/Rb ratios (Ogungbuyi *et al.*, 2022).

### 7.3.3 The origin of low Th/U ratios in the Namaqualand melilitites.

All Namaqualand melilitites display Th/U ratios that are lower than those of Bushmanland or other South African melilitites and kimberlites. The average  $(\text{Th}/\text{U})_{\text{PM}}$  ratio (i.e., Th/U normalised to primitive mantle) for the Namaqualand melilitites is  $0.27 \pm 0.10$  ( $1\sigma$ ) with a maximum Th/U ratio for the Waterval pipe of 0.49 and a minimum Th/U ratio for the BIES-D pipe of 0.12. The Bushmanland melilitites, in comparison, have an average  $(\text{Th}/\text{U})_{\text{PM}}$  ratio of  $1.00 \pm 0.17$  ( $1\sigma$ ), the Western Cape melilitites have a mean of  $1.04 \pm 0.10$  (Janney *et al.*, 2002) and South African kimberlites have an average of  $1.04 \pm 0.12$  (le Roex *et al.*, 2003; Becker and le Roex, 2006). Ocean island basalts have similar values.

### 7.3.4 Possible effect of perovskite fractionation.

The characteristic of low Th/U in Namaqualand melilitites was initially recognised by Rogers *et al.* (1992). They suggested, based on the fact that Namaqualand melilitites have both lower K/Nb and Th/U ratios than Bushmanland melilitites, that both of these characteristics were caused due to the

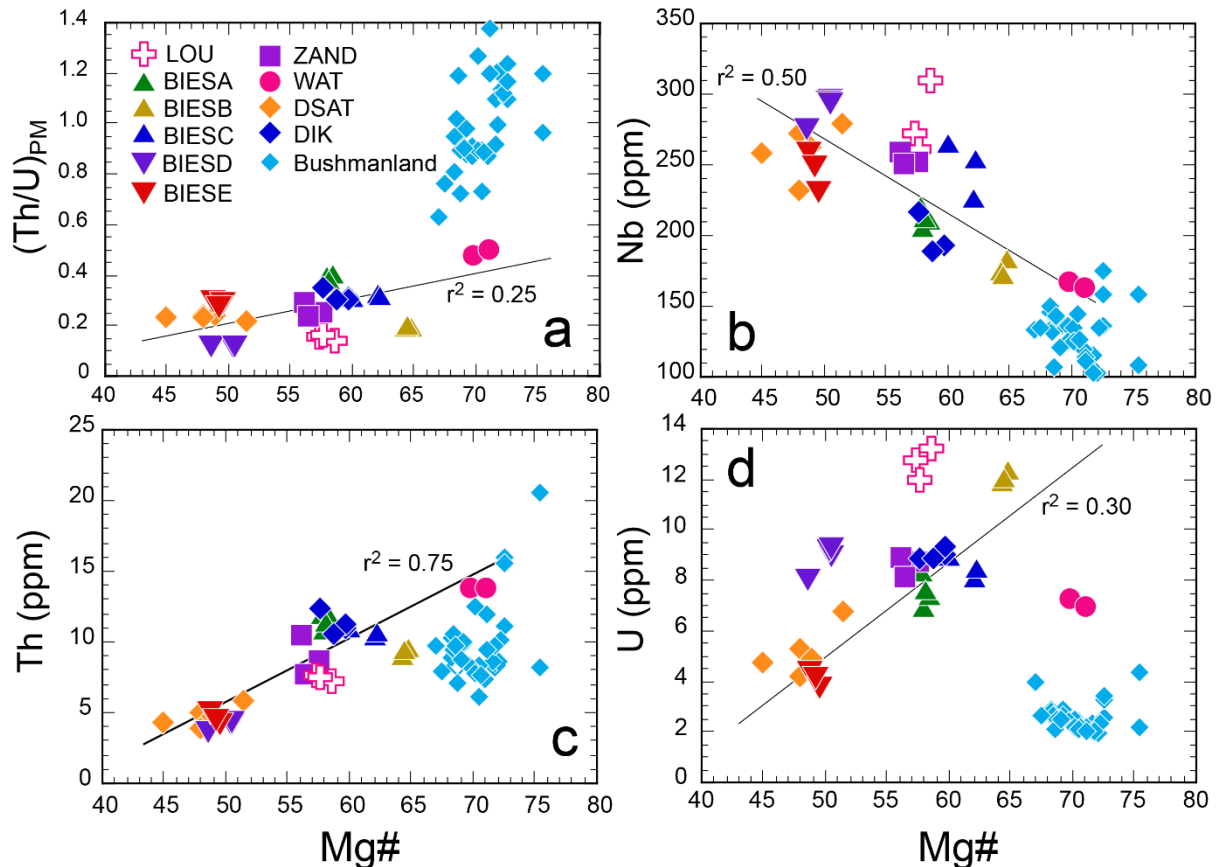


**Figure 64.** Mg, # (i.e.,  $100 \times [\text{Mg}/(\text{Mg} + \text{Fe}^{2+})]$  in atomic units) for the Namaqualand and Bushmanland melilitites versus (a) primitive mantle-normalised Th/U ratio, (b) Nb concentration in ppm, (c) Th concentration in ppm, and (d) U concentration in ppm. Regressions with correlation coefficients for the Namaqualand data are included in each panel. Note the decrease in U and Th contents and Th/U ratios with decreasing Mg# values. Nb is included for comparison as its incompatibility during mantle melting is nearly identical to that of U and Th.

presence of residual phlogopite in the mantle source of the Namaqualand melilitites and to its absence or relative scarcity as a residual mineral in the mantle source(s) of the Bushmanland melilitites.

More recent studies of Th and U partitioning between phlogopite and melt, however, do not support the idea that melting mantle assemblages containing residual phlogopite (or fractional crystallisation of phlogopite) can cause significant fractionation of Th/U ratios (e.g., La Tourrette *et al.*, 1995).

The hypothesis that the Th/U variations in Namaqualand are likely at least partly related to fractional crystallization is supported by the fact that Th/U ratios ( $r^2 = 0.25$ ) as well as Th and U concentrations ( $r^2 = 0.75$  and  $0.3$ , respectively) all correlate positively with Mg# (see Figure 64 above), meaning that the concentrations of both elements decrease with increasing fractionation. One mineral that may be capable of fractionating Th and U and decreasing their concentrations is perovskite. As shown in section 7.1.2 of this chapter, perovskite was likely a constituent (though minor) in most of the mineral assemblages that fractionally crystallized from the Namaqualand melilitites during their emplacement. Chakhmouradian *et al.* (2013) showed that perovskite D values for Th are 7 to 25 times higher than for U in kimberlites and other silica-deficient ultramafic magma types, such as katungites. Onuma *et al.* (1981) presented perovskite D values for Th and U in melilite nephelinites which are 4 times higher for Th than U. Therefore, perovskite fractionation can offer a simple explanation for the low Th/U ratios. Depending on the partition coefficients used (see Table 17 above), it requires between 1 and 5% perovskite fractionation to generate the range of Th/U values spanned by the Namaqualand melilitites, and between 1.5 and 7% to generate the full range of values spanned by both the Namaqualand and Bushmanland melilitites.

**Table 17. Mineral D values for Th and U in likely members of fractionating mineral assemblages.**

| Mineral Name | Mineral D values |       | Reference:                          |
|--------------|------------------|-------|-------------------------------------|
|              | D-Th             | D-U   |                                     |
| Olivine      | 0.01             | 0.01  | Lemarchand <i>et al.</i> , 1987     |
| CPX          | 0.57             | 0.55  | Onuma <i>et al.</i> , 1981          |
| Melilite     | 0.25             | 0.25  | Onuma <i>et al.</i> , 1981          |
| Magnetite    | 0.1              | 0.11  | Lemarchand <i>et al.</i> , 1987     |
| Perovskite   | 40               | 12    | Onuma <i>et al.</i> , 1981          |
| Perovskite   | 164              | 18    | Chakhmouradian <i>et al.</i> , 2013 |
| Nepheline    | 0.04             | 0.043 | Onuma <i>et al.</i> , 1981          |

However, it is important to point out that it is not only the Th/U ratio that distinguishes the Namaqualand and Bushmanland melilitites, but rather, also that U concentrations in the Namaqualand melilitites concentrations (particularly in the more primitive samples) extend to much higher values than those in Bushmanland. Therefore, the fact that the near-primary Waterval and other relatively unfractionated Namaqualand melilitites (e.g., BIESB) have such high U contents and low Th/U ratios cannot be plausibly explained by perovskite fractionation alone, but rather appears to be mainly a feature of the mantle source of these magmas.

### 7.3.5 Trend of decreasing Th/U with increasing latitude:

A unique feature observed within the Namaqualand and Bushmanland melilitites is a progressive increase in the Th/U ratio between the southern Namaqualand samples and the northern Bushmanland samples as illustrated in Figure 65. In addition to the variations in Th/U ratios in the Namaqualand melilitites as discussed above, there is also a significant northward increase in Th/U in the Bushmanland melilitites, whereas the Warmbad kimberlites show no clear gradient. The fact that the Bushmanland melilitites fall within a fairly narrow range of near-primary Mg# values (67 to 75) that do not correlate well with Th/U ratios (Figure 64a) indicates that perovskite fractionation is not a plausible explanation for the full variation in (Th/U)<sub>PM</sub> ratios (0.6 to 1.4; Janney *et al.*, 2017) however the fractionation of minerals like perovskite may have contributed to a minor extent. Although a full discussion of the cause of this variation in Th/U is outside the scope of this thesis, it is worth noting that there is also an apparent overall increase in enrichment in the most incompatible elements from south to north within the Bushmanland cluster, which may be related to the increase in Th/U (see Figure 62c). This observation raises the question of how the spatial distribution of the Namaqualand and Bushmanland could have resulted in the geochemical differences between the pipes.

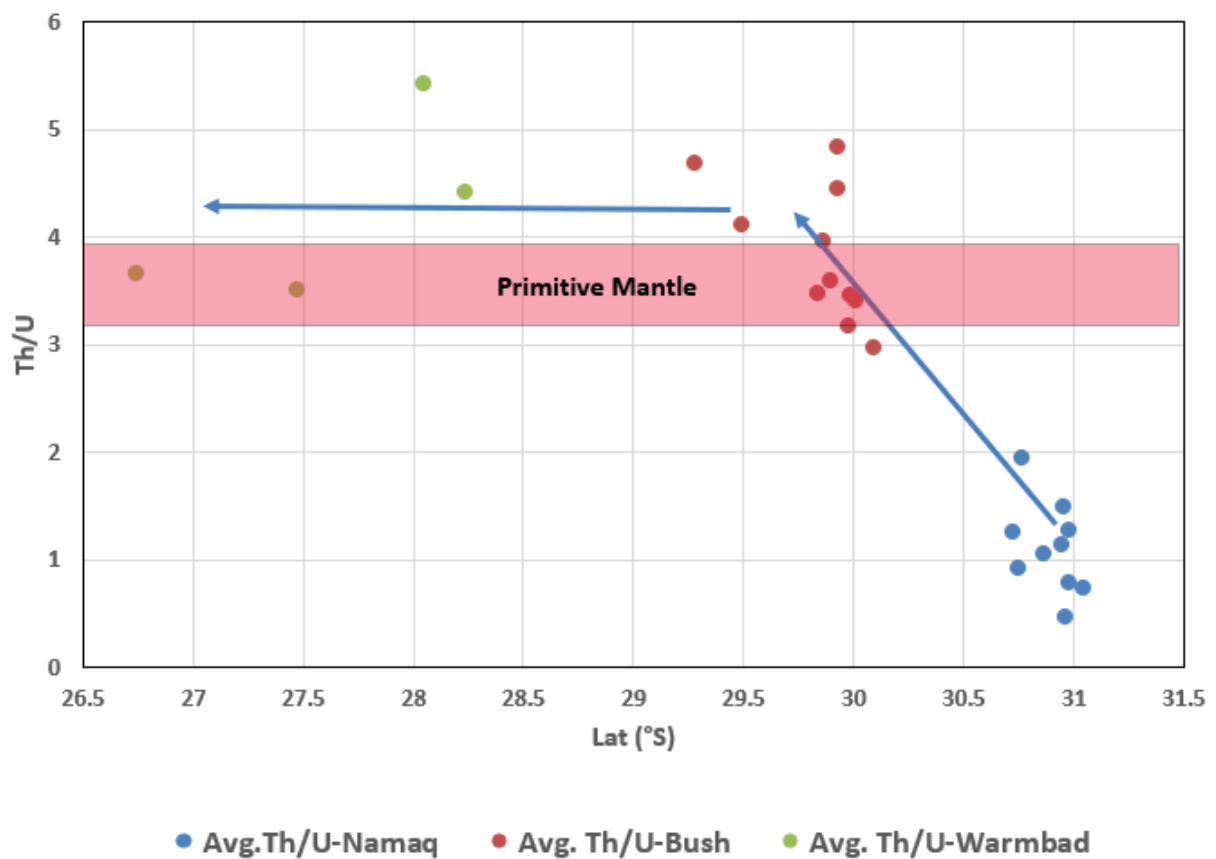


**Figure 65. Variation in Th/U ratio (average shown per pipe) for the Namaqualand, Bushmanland and Warmbad pipes studied. The Warmbad and Bushmanland data was obtained from Janney *et al.* (2017). The pink band is centred on the primitive mantle value of McDonough and Sun (1995).**

## 7.4. Radiogenic isotope constraints on the possible mantle source(s):

### 7.4.1 Spatial distribution of the HIMU signature in Namaqualand, Bushmanland and Warmbad clusters:

The Namaqualand melilitites have relatively uniform Sr-Nd isotope compositions that are similar to, but slightly higher in  $^{87}\text{Sr}/^{86}\text{Sr}_i$  (0.7031 - 0.7035) and lower in  $\epsilon_{\text{Nd}}(t)$  (+3.8 to +1.6) than the composition of the HIMU mantle endmember inferred from the compositions of basalts from ocean islands such as St. Helena in the South Atlantic and Tubuai and Mangaia in the South Pacific Ocean. However, the Pb isotope compositions of the Namaqualand melilitites span a wide range, extending from intermediate compositions similar to those designated for the "PREMA" and "FOZO" (or "C") mantle components (Zindler and Hart, 1986; Stracke *et al.*, 2005; Hanan and Graham, 1996, i.e., proposed to represent the typical composition of ambient deep convecting mantle material below the

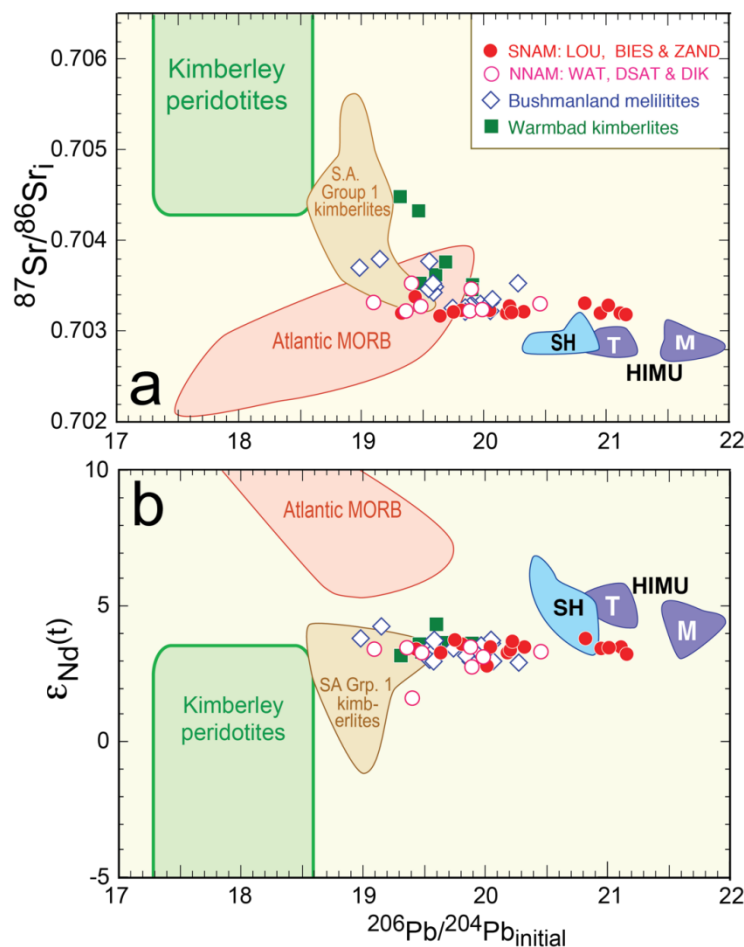


**Figure 66.** Initial  $^{206}\text{Pb}/^{204}\text{Pb}$  versus (a)  $^{87}\text{Sr}/^{86}\text{Sr}_i$  and (b)  $\epsilon_{\text{Nd}}(t)$ . Data shown include samples from pipes in the southern Namaqualand cluster (SNAM: LOU, BIESA-BIESE and ZAND) and the northern Namaqualand cluster (NNAM: WAT, DSAT and DIK), Bushmanland (including samples from 13 localities) and the Warmbad kimberlites (including samples from 4 localities). It should be noted that all Sr isotopic data shown have been obtained on leached sample powders, as this has been shown to be an effective way to mitigate alteration effects on Sr isotope ratios. Data for Bushmanland and Warmbad samples are from Janney *et al.* (2017). The source of data for Kimberley peridotites is Hawkesworth *et al.* (1990) source of data for other fields are the same as those given in Figure 59.

depleted upper mantle) to strong HIMU-type compositions even more radiogenic than those of OIB from St. Helena OIB and similar to those from Tubuai.

Moreover, there is a spatial relationship between the distribution of the HIMU signature. The southern and central Namaqualand pipes (e.g., LOU, BIES-A to BIES-E, ZAND) have the highest initial  $^{206}\text{Pb}/^{204}\text{Pb}$  values (range of 19.3-21.2 with a mean of  $20.3 \pm 0.6$  ( $1\sigma$ )), therefore, displaying the strongest HIMU signature; Figure 66), whereas those from the northern Namaqualand cluster (WAT, DSAT and DIK) have somewhat lower values (range = 19.1 - 20.5, mean =  $19.7 \pm 0.4$ ).

Further north, Pb isotope compositions of the Bushmanland melilitites are similar, on average to those of northern Namaqualand ( $^{206}\text{Pb}/^{204}\text{Pb}_i$  range = 19.0 - 20.3, mean =  $19.7 \pm 0.3$  ( $1\sigma$ )), but they extend to slightly higher initial  $^{87}\text{Sr}/^{86}\text{Sr}$  values (0.7032 - 0.7038; Janney *et al.*, 2017) but also slightly higher  $\epsilon_{\text{Nd}}(t)$  values (+2.8 to +4.3). The Warmbad kimberlites (excluding the  $\approx 510$  Myr Ondermatjie locality; Wu *et al.*, 2010) have similar, but still slightly lower average  $^{206}\text{Pb}/^{204}\text{Pb}_i$  values (range = 19.3 - 19.9, mean =  $19.6 \pm 0.2$ ) and extend to higher  $^{87}\text{Sr}/^{86}\text{Sr}_i$  (0.7034 - 0.7044), although with  $\epsilon_{\text{Nd}}(t)$  values similar to Bushmanland and Namaqualand melilitites (+2.9 to +4.3; Figure 66).

#### **7.4.2 Correlation of isotopic composition with lithospheric thickness, as model for the origin of the NBW lineament:**

The spatial pattern of decreasing average  $^{206}\text{Pb}/^{204}\text{Pb}_i$  and increasing  $^{87}\text{Sr}/^{86}\text{Sr}_i$  from southwest to northeast in the NBW province (as shown in Figure 66) roughly correlates with estimates of lithospheric thickness along the NBW lineament, from  $\approx 140$  km beneath the coastal region at Namaqualand to more than 160 km thickness in the interior beneath the Warmbad cluster in the interior (Figure 67). This trend may also be influenced by the assimilation of different crustal material or due to different degrees of crustal assimilation between the northern and southern pipes.

The pattern of isotopic composition varying with lithospheric thickness is very similar to that shown by the Western Cape melilitite province (WCMP) that extends from submarine alkali basalts on the Agulhas Bank to olivine melilitites at Sutherland and Salpeterkop nearly 250 km inland (Janney *et al.*, 2002). This province includes 5 localities that show a general decrease in  $^{206}\text{Pb}/^{204}\text{Pb}_i$  and  $\epsilon_{\text{Nd}}(t)$  and an increase in  $^{87}\text{Sr}/^{86}\text{Sr}_i$  from the continental shelf, to the southern coastal region to the interior in the southern Karoo. Also, like the NBW province, they span an age from Late Cretaceous to Palaeogene and are age-progressive, with the age of volcanism increasing from north to south at a rate approximately consistent with African plate motion at this time.

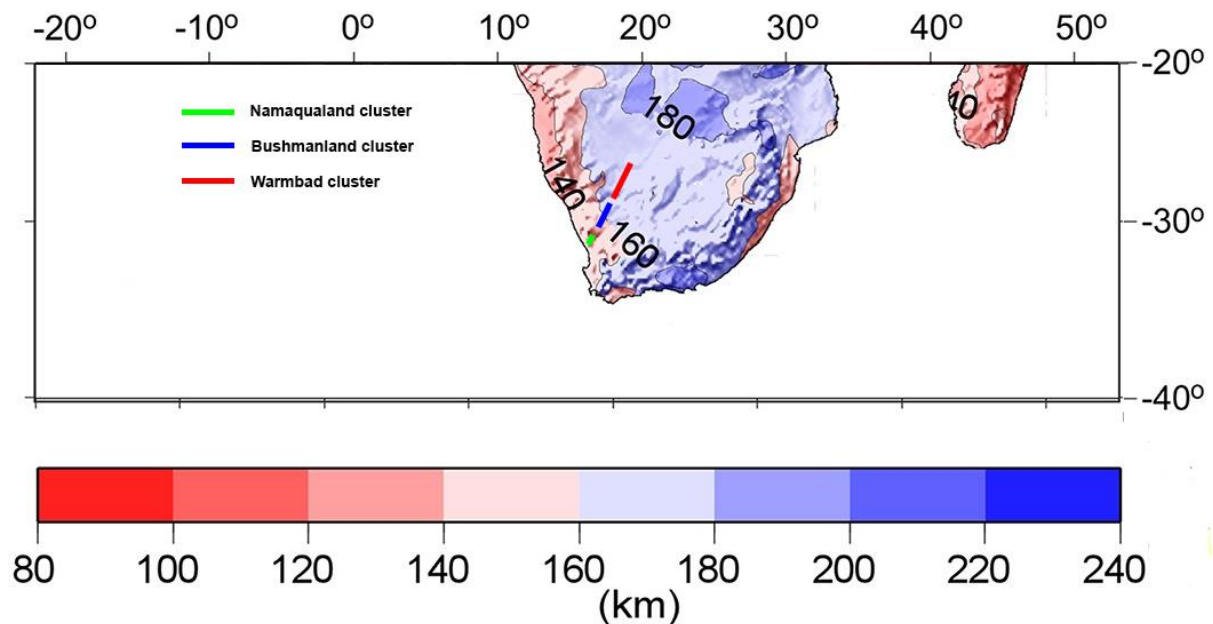


**Figure 67. Estimates of lithospheric thickness beneath southern Africa based on seismological constraints, from Globig *et al.* (2016). Note the apparent increase in lithospheric thickness from the coast to the interior along the NBW lineament.**

Janney *et al.* (2002) explained the WCMP as representing the trace of a small, relatively short-lived plume or hotspot, possibly related to the southern African "superplume" (Gurnis *et al.*, 2000), cutting across the Western Cape region and active from the Late Cretaceous to Palaeogene. They further proposed that the strong HIMU affinity of basalts and melilitites from the WCMP was derived from this sublithospheric plume feature, but that this was variably diluted by mixing with lithospheric peridotite to varying degrees: more in areas of thick lithosphere and less in areas of thin lithosphere.

Lithospheric peridotite was envisioned to have a broadly "enriched mantle" type isotopic characteristics with relatively high  $^{87}\text{Sr}/^{86}\text{Sr}$ , low  $\epsilon_{\text{Nd}}(t)$  and low to moderate  $^{206}\text{Pb}/^{204}\text{Pb}$  similar to the compositions measured in whole-rock southern African peridotites (e.g., Hawkesworth *et al.*, 1990). Such a model would seem to also apply well to the origin of the age-progressive, Late Cretaceous to Palaeogene Namaqualand-Bushmanland-Warmbad igneous lineament. This is depicted in the cartoon in Figure 68, where the three magmatic clusters form as the result of a single small, "plumelet" feature remaining stationary in the mantle reference frame and generating melts while the southwestern African plate moves over it.

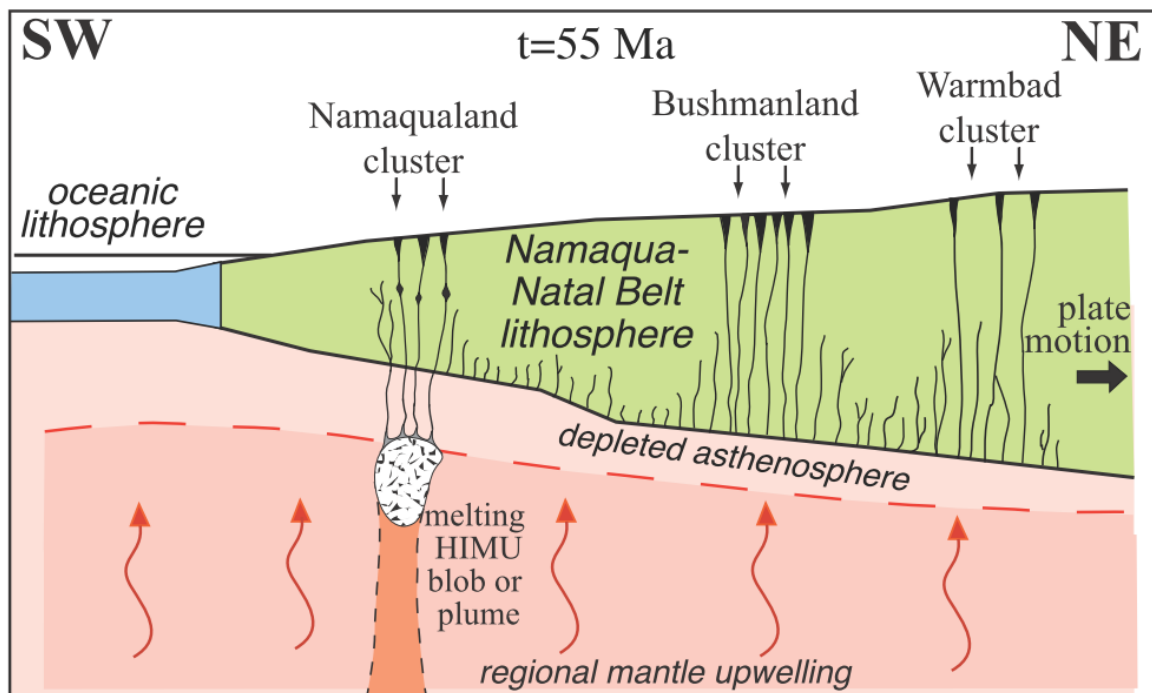


**Figure 68.** Cartoon cross-section through the Namaqualand-Bushmanland-Warmbad lineament at 55 Ma during emplacement of the Namaqualand melilitite pipes. A blob or plumelet of HIMU isotopic affinity undergoes melting and these melts encounter the lithospheric mantle where they percolate upward and progressively assimilate metasomatized lithospheric peridotite (with this assimilation being proportional to the thickness of lithosphere traversed). The small swellings in the Namaqualand pipes simply designate that these pipes have experienced variable differentiation (actual magma chambers being unlikely as these would have allowed extensive degassing of the melilitites magmas, which seems not to have occurred). Precisely why this differentiation occurs presumably has to do with local conditions in the Namaqualand lithosphere. Figure adapted from Janney *et al.* (2002).

There are two potential problems with the above hypothesis. The first is that, as with the Western Cape melilitite province, there is no known young or active volcanism in the south-eastern Atlantic that could represent the recent activity of the plume(let) envisioned to be responsible for the NBW lineament (O'Connor and le Roex, 1992).

This is not necessarily a serious problem as there are many examples of short-lived linear volcanic chains in the ocean basins, particularly appreciated with superplume features (e.g., Koppers *et al.*, 2003). The second problem is potentially more serious, and that is that the NBW lineament appears to be the continuation of a much larger,  $\approx 2500$  km long alkaline magmatic lineament extending NE from the Namaqualand coast across southern Africa and reaching the southern extent of the East African Rift system (EARS; Moore *et al.*, 2008 Figure 69). This feature was called the "African kimberlitic megalineament" by Janney *et al.* (2017). Aside from the NBW portion, this alkaline magmatic lineament is not age-progressive but rather is dominated by kimberlites that range between 90 and 110 Ma in age (Figure 69).

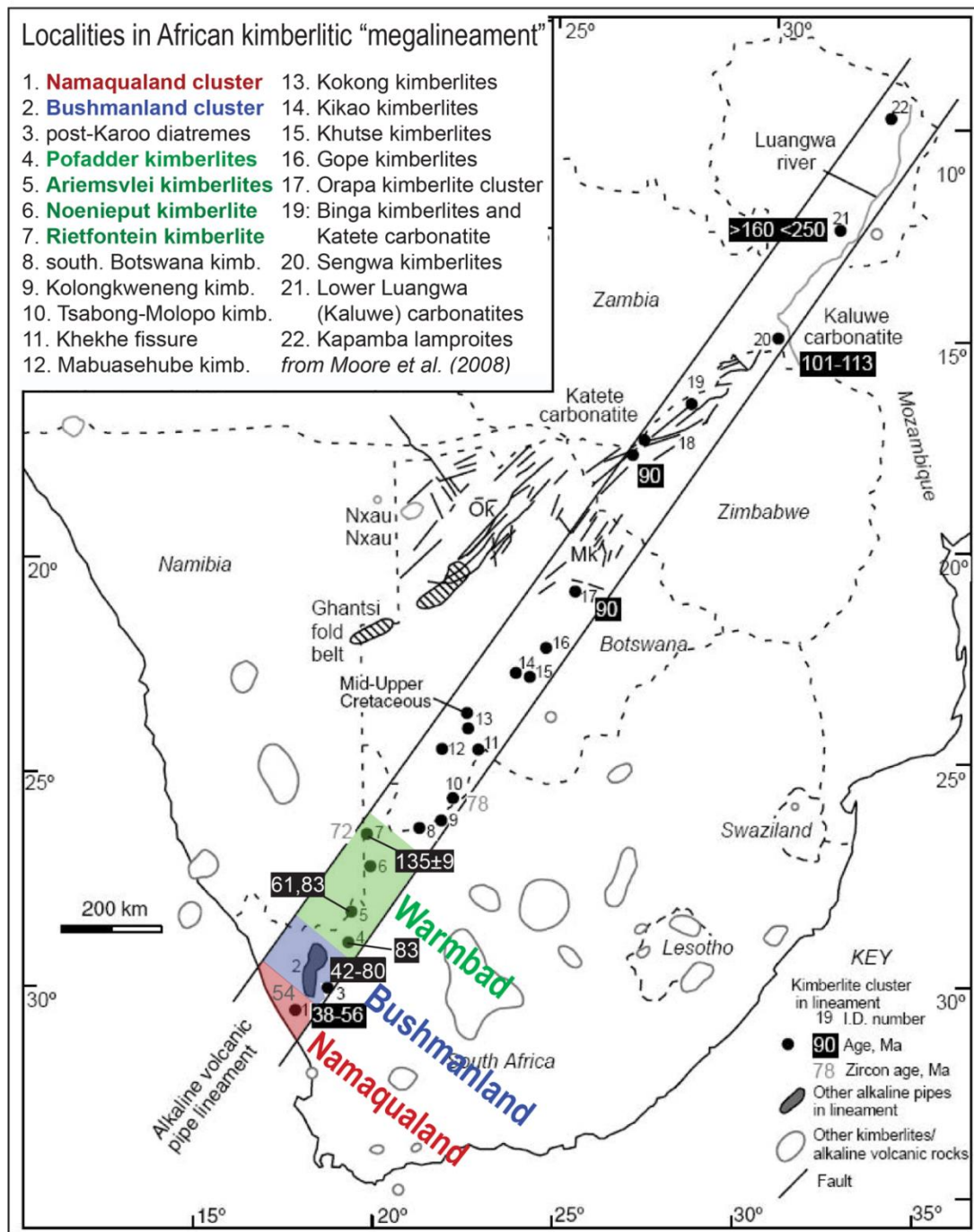


**Figure 69. Map of southern Africa showing clusters of kimberlite and other alkaline magmatic activity. The "African kimberlitic megalineament" is shown between the two parallel NE-SW oriented lines and this shows the relationship of this feature to the Namaqualand-Bushmanland-Warmbad province of South Africa and Namibia. Figure adapted from Moore et al. (2008).**

Moore *et al.* (2008) proposed that this lineament was the result of lithospheric stresses rather than processes occurring in the lower mantle. Some support for this hypothesis is provided by recent plate motion studies revealing that there is an extensional plate boundary running between the west coast of southwestern Africa and the southern Malawi Rift (the southernmost part of the EARS; Wedmore *et al.*, 2021). Based on this evidence, the hypothesis that the African kimberlitic megalineament, and by extension the NBW province, were the products of incipient rifting or other lithospheric stresses seems plausible. Major unanswered questions are (1) why should such rifting or stresses produce age-

progressive magmatism in one area and diffuse, roughly simultaneous magmatism in others and (2) if extensional activity sufficient to initiate magmatism began 100 Myr ago or more, why does the evidence of lithospheric extension remain so cryptic today, as there is no clear surface expression (such as rift valleys) along the entire length of the megalineament. However, these questions are outside the scope of this thesis.

An argument can be made that the formation of the larger “African megalineament” could be related to the same plume that caused the NBW lineament by triggering a zone of more extensive magmatism along a deep-seated lithospheric mantle zone of weakness from Southern Africa into the east African rift zone.

Furthermore, a physical mechanism has yet to be found to explain why the olivine melilitites in the thinner Namaqualand crust seemingly have experienced greater degrees of olivine fractionation compared to the Bushmanland cluster. However, it is speculated that this could be in some way related to the difference in thickness between the Namaqualand and Bushmanland regions to allow for more rapid fractional crystallization of olivine, and/or for longer residence times in the crust prior to the eruption of the diatremes. The evidence shown supports the suggestions for an intermediate magma chamber, where rapid fractional crystallization would occur, to differentiate the magmas by the required amount before their emplacement in diatremes. However further elaboration of this lies beyond the scope of this study.

## 8. CONCLUSION:

This study has focused on the petrography and geochemistry of 43 fresh igneous rocks sampled from 10 closely spaced magmatic pipes. It has helped to reveal significantly more information about this relatively young (35-56 Ma) melilitite pipe cluster in Namaqualand. The lineament consisting of the Namaqualand pipe cluster (including the Zandkopsdrift carbonatite) as well as related Bushmanland and Warmbad pipe clusters, collectively form the most recent (35-80 Ma) and densest concentration of mafic alkaline magmatism in southern Africa. This lineament is especially enigmatic since it shows an age progression from the Late Cretaceous Bushmanland/Warmbad melilitite and kimberlite pipes in the northeast to the Paleogene-age Namaqualand melilitite pipes in the southwest. This age-progressive path is roughly consistent with Late Cretaceous to Cenozoic African plate motion. The precise cause of the 400 km long NNE-SSW trending age progressive NBW magmatic province/lineament remains elusive. Geochemical evidence suggests the involvement of a HIMU-like blob/plume possibly originating from a broad mantle upwelling located beneath southern Africa that may be related to incipient rifting as part of the larger “African megalineament”.

Beyond investigating the origin of the Namaqualand cluster and the NBW lineament as a whole, this thesis has revealed that the Namaqualand melilitites are petrologically anomalous. The mineralogy of the samples was determined by optical microscopy and samples were geochemically classified into three broad rock types (olivine melilitites, olivine nephelinites and nephelinites). These rock types exhibit a range in mineral abundances reflected by their diverse chemistry and show a range in textures from coarse to fine that is likely to be an effect of different rates of cooling.

They have compositions that are significantly more differentiated than the vast majority of diatreme-hosted, mantle-derived igneous rocks globally. This makes the Namaqualand cluster of melilitites a feature of importance for understanding igneous petrology within the continental margin tectonic setting. The Namaqualand melilitites show Mg#s from ~71 down to values as low as 45, with an average of 57.2. They also show an unusual extent of SiO<sub>2</sub> under-saturation as well as relatively Ti and Fe rich compositions. Their SiO<sub>2</sub> contents varies from 30 to 36 wt. %, which is anomalously low and this high degree of SiO<sub>2</sub> undersaturation would result in a decrease in SiO<sub>2</sub> during olivine fractionation. This is unusual as olivine fractionation usually drives SiO<sub>2</sub> for most igneous rocks.

The discovery in the course of this research of a near-primary melilitite pipe from farm Waterval in the Namaqualand cluster as well as the abundance of olivine phenocrysts in these rocks strongly supports the hypothesis that the Namaqualand melilitites were formed by the evolution of primary magmas by fractional crystallization dominated by olivine crystallization. Two approaches were used to model the fractionation history of the Namaqualand melilitites. A). Assumes that olivine was the sole mineral in the fractionating assemblage and uses calculated equilibrium olivine compositions to iteratively correct the modelled composition. B). A wider range of fractionating minerals is employed using the least-squares modelling approach. Both of these simplistic approaches help provide a rough constraint on the fractionation history of these pipes. Unfortunately, more realistic fractionation

modelling, using codes such as pMELTS or Pele, was not feasible because these programs are not capable of dealing with these types of silica-undersaturated magma compositions.

Virtually all igneous rocks occurring in diatremes elsewhere (including the nearby Bushmanland and Warmbad clusters) have compositions approaching those of primary magmas while these extremely undersaturated compositions extend to relatively evolved compositions.

By applying fractional crystallization modelling, the Mg#s of the Namaqualand melilitites were corrected to a primary composition of 73, which showed that the Namaqualand melilitites could have experienced between 6 and to as much as 60% fractionation of equilibrium olivine. In contrast, the Bushmanland pipes only require only up to 10% olivine fractionation to bring their Mg# values up to 73. The extreme degree of olivine fractional crystallization for the Namaqualand pipes is unusual when considering that these magmas are predicted to rise very rapidly through the lithospheric crust to surface from their source regions driven by volatile exsolution combined with a relatively low magma viscosity. The exact mechanism to support the expected rapid eruption of these pipes with the simultaneous extreme degrees of fractional crystallization leaves a challenging question to be answered by future studies.

This study of the Namaqualand melilitites revealed exceptionally low  $\delta^{18}\text{O}$  values (i.e., down to +4.2 ‰) within three melilitite pipes emplaced within the mid-Cretaceous Koegel Fontein igneous complex. This is contrasted by the higher  $\delta^{18}\text{O}$  values for olivines from the majority of the melilitite pipes which were indistinguishable from typical upper mantle peridotite (+4.9 to +5.2‰). Coincidentally the crustal country rocks surrounding the Koegel Fontein complex, as well as igneous rocks associated with it that have been strongly contaminated by this crust, have exceptionally low  $\delta^{18}\text{O}$  values (down to -4 and -5.3‰, respectively). Therefore, the unusually low- $\delta^{18}\text{O}$  values of these olivines could be explained by assimilation of up to 10% of Koegel Fontein complex-related crustal rock with the lowest known  $\delta^{18}\text{O}$  values. It remains unclear whether the modelled degree crustal assimilation suggested by the low  $\delta^{18}\text{O}$  olivines for melilitites emplaced within the Koegelfontein complex, is typical of all the Namaqualand melilitites.

A common source and petrogenesis for the Namaqualand melilitites are supported by the relatively uniform concentrations of most incompatible trace elements, however low Pb concentrations in the Namaqualand melilitites, along with their  $\text{SiO}_2$  poor major element compositions make it unlikely that they experienced significant (e.g., more than 5-10%) assimilation of local continental crust. Larger amounts of crustal assimilation are not supported by this study, as they would result in detectable increases in  $\text{SiO}_2$  and Pb/Ce ratios. The Namaqualand melilitites are characterized by extraordinarily high and variable Nb/Rb and U/Th ratios, and correlations with other elements, indicate that these ratios have been affected by variable fractional crystallization of phlogopite and perovskite, respectively. This cannot explain the unusually high U concentrations and low Th/U ratios that appear to be mainly a source-derived feature seen in the most primitive magmas.

The Namaqualand melilitites have radiogenic isotope compositions overlapping with those of melilitites and kimberlites from the Bushmanland and Warmbad clusters, as well as with southern

African Group I kimberlites. However, another interesting aspect revealed by this study is that the Namaqualand pipes are unique in that the southernmost pipes have radiogenic isotope values closest to those of HIMU oceanic island basalts (e.g., from St. Helena, Mangaia, Tubuai), whereas the northernmost Namaqualand pipes, as well as the Bushmanland and Warmbad clusters, display isotopic compositions that only extend to weaker HIMU signatures.

The geochemical and age-distance patterns displayed by the NBW igneous rocks are most consistent with the action of a mantle plume passing beneath the western margin of southern Africa in the Late Cretaceous to Paleogene. This is the simplest explanation for the generation of the NBW lineament as it is consistent with the fact that the samples with the strongest HIMU signatures in the NBW lineament are those that have been emplaced on the thinnest lithosphere, nearest the continental margin (southern Namaqualand cluster). The HIMU signature dominant in the Namaqualand melilitites is presumably related to the plume source. The potential for the NBW lineament to also be related to incipient rifting cannot be ruled out, however the age progression along this lineament creates some controversy for rifting alone being the sole cause of the African megalineament as the involvement of a plume/blob of HIMU like composition seems necessary to explain the age progression.

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## 10. APPENDIX:

### 10.1. Appendix A: List of Samples by Locality:

Petrographic summary of the samples collected during the study from the 9 pipes sampled.

**Appendix A Table 18. List of Samples collected, rock types, date, locality and Co-ordinates.**

| Pipe   | Sample Name | Rock Type                                                            | Date   | Locality Name         | Location (Need to check) |
|--------|-------------|----------------------------------------------------------------------|--------|-----------------------|--------------------------|
| BIES A | BIES-10     | Partially altered olivine nephelinite                                | 1970s  | Biesiesfontein Pipe A | Unknown                  |
|        | BIES-11     | Partially altered medium grained olivine nephelinite                 | 6-2013 | Biesiesfontein Pipe A | 30°57.395'/17°58.703'    |
|        | BIESA-1     | Partially altered fine acicular olivine nephelinite                  | 3-2014 | Biesiesfontein Pipe A | 30°57.392'/17°58.703     |
|        | BIESA-2     | Partially altered fine acicular olivine nephelinite                  | 3-2014 | Biesiesfontein Pipe A | 30°57.392'/17°58.703     |
|        | BIESA-VM1   | Partially altered vesicular olivine nephelinite.                     | 3-2014 | Biesiesfontein Pipe A | 30°57.392'/17°58.703     |
|        | BIESA-VM2   | Partially altered vesicular orthoclase bearing melilitite            | 3-2014 | Biesiesfontein Pipe A | 30°57.392'/17°58.703     |
| BIES B | BIESA-CR1   | Medium grained granite                                               | 3-2014 | Farm Biesiesfontein   | 30°57.385/17°58.737      |
|        | BIESB-1     | Fresh porphyritic cpx olivine melilitite                             | 3-2014 | Biesiesfontein Pipe B | 30°58.830'/17°56.096     |
|        | BIESB-2     | Fresh porphyritic cpx olivine melilitite                             | 3-2014 | Biesiesfontein Pipe B | 30°58.830'/17°56.096     |
|        | BIESB-3     | Fresh porphyritic olivine melilitite                                 | 3-2014 | Biesiesfontein Pipe B | 30°58.830'/17°56.096     |
| BIES C | BIESC-1     | Fresh flow textured olivine clinopyroxene melilitite                 | 3-2014 | Biesiesfontein Pipe C | 30°59.004'/17°58.363     |
|        | BIESC-2     | Altered flow textured olivine melilitite                             | 3-2014 | Biesiesfontein Pipe C | 30°59.004'/17°58.363     |
|        | BIESC-3     | Fresh flow textured olivine clinopyroxene melilitite                 | 3-2014 | Biesiesfontein Pipe C | 30°59.004'/17°58.363     |
| BIES D | BIESD-1     | Partially altered olivine clinopyroxene nephelinite                  | 3-2014 | Biesiesfontein Pipe D | 30°58.218/17°58.712'     |
|        | BIESD-2     | Fresh olivine clinopyroxene nephelinite                              | 3-2014 | Biesiesfontein Pipe D | 30°58.218/17°58.712'     |
|        | BIESD-3     | Extensively altered olivine clinopyroxene nephelinite                | 3-2014 | Biesiesfontein Pipe D | 30°58.210/17°58.618      |
|        | BIESD-4     | Partially altered olivine clinopyroxene nephelinite                  | 3-2014 | Biesiesfontein Pipe D | 30°58.210/17°58.618      |
|        | BIESD-CR1   | Fine-grained to medium grained granite/granophyre                    | 3-2014 | Farm Biesiesfontein   | 30°58.246/17°58.718      |
|        | BIESD-CR2   | Medium grained graphic granite/granophyre                            | 3-2014 | Farm Biesiesfontein   | 30°58.181/17°58.662      |
|        | BIESE-1     | Partially altered olivine clinopyroxene nephelinite                  | 7-2014 | Biesiesfontein Pipe E | 30°57.231/17°56.651      |
| BIES E | BIESE-2     | Slightly altered olivine clinopyroxene nephelinite                   | 7-2014 | Biesiesfontein Pipe E | 30°57.231/17°56.651      |
|        | BIESE-3     | Partially altered olivine clinopyroxene nephelinite                  | 7-2014 | Biesiesfontein Pipe E | 30°57.231/17°56.651      |
| DIK    | DIK-10      | Fresh porphyritic olivine melilitite                                 | 1970s  | Dikdoorn main pipe    | Unknown                  |
|        | DIK-11      | Fresh altered fine grained clinopyroxene nephelinite                 | 6-2013 | Dikdoorn main pipe    | 30°43.710'/17°59.516'    |
|        | DIK-12      | Fresh Olivine Melilitite                                             | 6-2013 | Dikdoorn main pipe    | 30°43.710'/17°59.516'    |
|        | DIK-13      | Fresh Olivine Melilitite                                             | 3-2014 | Dikdoorn main pipe    | 30°43.711/17°58.532      |
|        | DIK-VM1     | Altered Amygdaloidal Olivine Melilitite                              | 3-2014 | Dikdoorn main pipe    | 30°43.711/17°58.532      |
|        | DIK-VM2     | Altered Amygdaloidal Olivine Melilitite                              | 3-2014 | Dikdoorn main pipe    | 30°43.711/17°58.532      |
|        | DIK-VM3     | Foliated Amygdaloidal Lapilli bearing Olivine Melilitite             | 3-2014 | Dikdoorn main pipe    | 30°43.711/17°58.532      |
|        | DIK-VM4     | Altered Amygdaloidal Olivine Melilitite                              | 3-2014 | Dikdoorn main pipe    | 30°43.711/17°58.532      |
|        | DIK-CR1     | Medium grained granite                                               | 3-2014 | Farm Dikdoorn         | 30°43.691/17°59.453      |
| DSAT   | DSAT-1      | Fine-grained Fresh acicular clinopyroxene nephelinite                | 7-2014 | Dikdoorn Sat. Pipe    | 30°45.178/17°57.135      |
|        | DSAT-2      | Slightly altered acicular sodalite clinopyroxene olivine nephelinite | 7-2014 | Dikdoorn Sat. Pipe    | 30°45.178/17°57.135      |
|        | DSAT-3A     | Fresh acicular sodalite clinopyroxene olivine nephelinite            | 7-2014 | Dikdoorn Sat. Pipe    | 30°45.178/17°57.135      |
|        | DSAT-3B     | Fresh acicular clinopyroxene olivine nephelinite                     | 7-2014 | Dikdoorn Sat. Pipe    | 30°45.178/17°57.135      |
|        | DSAT-4      | Slightly altered acicular clinopyroxene olivine nephelinite          | 7-2014 | Dikdoorn Sat. Pipe    | 30°45.171/17°57.121      |
|        | DSAT-CR1    | Medium grained, weakly foliated gneiss                               | 7-2014 | Farm Dikdoorn         | 30°45.153/17°57.135      |
| LOU    | LOU-1       | Altered acicular alkali basalt                                       | 7-2014 | Farm Louisfontein     | 31°02.771/18°02.327      |
|        | LOU-2       | Medium grained porphyritic olivine melilitite                        | 7-2014 | Louisfontein pipe     | 31°02.771/18°02.327      |
|        | LOU-3       | Fresh medium grained olivine melilitite                              | 7-2014 | Louisfontein pipe     | 31°02.771/18°02.327      |
|        | LOU-4       | Fresh coarse grained olivine melilitite                              | 7-2014 | Louisfontein pipe     | 31°02.771/18°02.327      |
|        | LOU-CR-1    | Coarse grained granite gneiss                                        | 7-2014 | Farm Louisfontein     | 31°02.771/18°02.327      |
| WAT    | WAT-1       | Altered medium grained porphyritic olivine melilitite                | 3-2014 | Waterval pipe         | 30°46.295/17°57.607      |
|        | WAT-2       | Poorly sorted medium grained porphyritic olivine melilitite          | 3-2014 | Waterval pipe         | 30°46.295/17°57.614      |
|        | WAT CR1     | Weakly foliated leco-gneiss.                                         | 3-2014 | Farm Waterval         | 30°46.295/17°57.607      |
|        | WAT CR2     | Banded amphibole, plagioclase gneiss                                 | 3-2014 | Farm Waterval         | 30°46.295/17°57.614      |
|        | RTPT-1      | Coarse Rietpoort granite                                             | 3-2014 | Biesiesfontein        | Quarry on Biesiesfontein |

## 10.2. Appendix B: Electron Microprobe Analysis of Individual Mineral Grains:

Appendix B Table 19: A collection of the results for the olivine crystals analysed by electron microprobe.

| Name    | Zone | Area* | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO   | MnO   | MgO   | CaO   | NiO   | Total |
|---------|------|-------|------------------|------------------|--------------------------------|--------------------------------|-------|-------|-------|-------|-------|-------|
| LOU-3   | ol 1 | r     | 39.38            | 0.1039           | 0.0184                         | -                              | 14.78 | 0.487 | 44.41 | 0.821 | 0.056 | 100.1 |
| LOU-3   | ol 1 | c     | 39.21            | 0.0657           | 0.0399                         | -                              | 17.5  | 0.268 | 42.87 | 0.31  | 0.123 | 100.4 |
| LOU-3   | ol 2 | r     | 39.84            | 0.078            | 0.0115                         | 0.0013                         | 15.22 | 0.439 | 44.25 | 0.676 | 0.074 | 100.6 |
| LOU-3   | ol 2 | o.Z.  | 39.26            | 0.031            | 0.0578                         | 0.007                          | 17.61 | 0.315 | 42.39 | 0.243 | 0.1   | 100.0 |
| LOU-3   | ol 2 | i.Z.  | 39.84            | 0.0778           | 0.0589                         | 0.0558                         | 16.67 | 0.25  | 43.45 | 0.172 | 0.245 | 100.8 |
| LOU-3   | ol 2 | r 2   | 39.15            | 0.0475           | 0.0626                         | 0.0457                         | 16.82 | 0.184 | 43.52 | 0.163 | 0.206 | 100.2 |
| LOU-3   | ol 2 | c     | 39.25            | 0.0602           | 0.052                          | 0.0381                         | 18.03 | 0.189 | 43.09 | 0.188 | 0.175 | 101.1 |
| LOU-3   | ol 2 | c 2   | 39.27            | 0.1087           | 0.0496                         | 0.0644                         | 16.97 | 0.202 | 43.49 | 0.191 | 0.215 | 100.6 |
| LOU-3   | ol 3 | r     | 40.02            | 0.1002           | 0.0273                         | 0.0183                         | 14.62 | 0.425 | 44.26 | 0.758 | 0.047 | 100.3 |
| LOU-3   | ol 3 | c     | 39.41            | 0.0464           | 0.0267                         | 0.0223                         | 17.51 | 0.198 | 43.38 | 0.187 | 0.181 | 101.0 |
| LOU-3   | ol 3 | c 2   | 39.36            | 0.0456           | 0.044                          | 0.043                          | 17.33 | 0.328 | 43.13 | 0.32  | 0.117 | 100.7 |
| LOU-3   | ol 4 | r     | 39.31            | 0.1211           | 0.0325                         | -                              | 14.57 | 0.479 | 44.26 | 0.921 | 0.051 | 99.7  |
| LOU-3   | ol 4 | c     | 39.27            | 0.0612           | 0.0197                         | -                              | 18.11 | 0.222 | 42.09 | 0.238 | 0.159 | 100.2 |
| LOU-3   | ol 5 | r     | 39.62            | 0.0773           | 0.0295                         | -                              | 16.63 | 0.303 | 43.07 | 0.448 | 0.13  | 100.3 |
| LOU-3   | ol 5 | c     | 39.37            | 0.0814           | 0.0424                         | -                              | 17.52 | 0.329 | 42.39 | 0.281 | 0.172 | 100.2 |
| LOU-3   | ol 6 | r     | 39.67            | 0.177            | 0.0446                         | -                              | 14.57 | 0.479 | 44.2  | 0.888 | 0.054 | 100.1 |
| LOU-3   | ol 6 | c     | 39.1             | 0.0405           | 0.0812                         | 0.0358                         | 18.8  | 0.273 | 41.71 | 0.285 | 0.134 | 100.5 |
| BIESE-1 | ol 1 | c     | 38.81            | 0.0637           | 0.0212                         | 0.0036                         | 18.46 | 0.314 | 41.85 | 0.386 | 0.013 | 99.9  |
| BIESE-1 | ol 2 | c     | 38.85            | 0.0794           | 0.047                          | 0.0152                         | 19.72 | 0.296 | 41.29 | 0.248 | 0.034 | 100.6 |
| BIESE-1 | ol 3 | r     | 38.89            | 0.1231           | 0.0356                         | -                              | 20    | 0.385 | 40.99 | 0.351 | -     | 100.8 |
| BIESE-1 | ol 3 | r     | 38.87            | 0.1404           | 0.0492                         | 0.0029                         | 19.26 | 0.427 | 40.94 | 0.57  | 0.019 | 100.3 |
| BIESE-1 | ol 3 | c     | 38.92            | 0.0296           | 0.0675                         | 0.0069                         | 18.59 | 0.283 | 42.26 | 0.182 | 0.016 | 100.4 |
| BIESE-1 | ol 3 | c     | 38.98            | 0.1134           | 0.0713                         | 0.0069                         | 18.84 | 0.254 | 41.85 | 0.209 | 0.064 | 100.4 |
| BIESE-1 | ol 4 | c     | 38.42            | 0.0059           | 0.0357                         | 0.0215                         | 19.62 | 0.416 | 40.03 | 0.64  | 0.002 | 99.2  |
| BIESE-1 | ol 4 | c     | 38.73            | 0.0425           | 0.0358                         | 0.0135                         | 20    | 0.275 | 41    | 0.229 | 0.028 | 100.4 |
| BIESE-1 | ol 5 | r     | 38.65            | 0.0268           | 0.0339                         | 0.0219                         | 22.06 | 0.495 | 36.2  | 1.002 | -     | 98.5  |
| BIESE-1 | ol 5 | r     | 38.89            | 0.0281           | 0.0532                         | -                              | 19.76 | 0.446 | 40.57 | 0.453 | 0.054 | 100.3 |
| BIESE-1 | ol 5 | c     | 39.01            | -                | 0.054                          | -                              | 19.69 | 0.228 | 41.46 | 0.269 | 0.095 | 100.8 |
| BIESE-1 | ol 5 | c     | 38.7             | 0.0605           | 0.0328                         | 0.0049                         | 19.75 | 0.266 | 41.08 | 0.282 | 0.006 | 100.2 |
| BIESE-1 | ol 6 | r     | 38.51            | 0.2138           | 0.0114                         | -                              | 21.91 | 0.634 | 38.19 | 1.15  | 0.038 | 100.7 |
| BIESE-1 | ol 6 | c     | 38.95            | 0.0286           | 0.0365                         | 0.0067                         | 19.47 | 0.337 | 40.84 | 0.325 | 0.06  | 100.1 |

\*

r=rim

c=core

i=inner

z=zone

o=outer

**Appendix B Appendix B Table 19 continued: A collection of the results for the olivine crystals analysed by electron microprobe.**

| Name   | Zone | Area* | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO   | MnO    | MgO   | CaO    | NiO    | Total    |
|--------|------|-------|------------------|------------------|--------------------------------|--------------------------------|-------|--------|-------|--------|--------|----------|
| WAT-1  | ol 1 | c     | 40.68            | 0.0298           | 0.0311                         | 0.0427                         | 13.74 | 0.1514 | 44.84 | 0.1799 | 0.2236 | 99.9185  |
| WAT-1  | ol 2 | c     | 39.93            | -                | 0.0725                         | 0.0854                         | 12.55 | 0.1969 | 47.06 | 0.1623 | 0.1936 | 100.2507 |
| WAT-1  | ol 3 | c     | 40.03            | 0.0137           | 0.0534                         | 0.0932                         | 12.71 | 0.1449 | 46.88 | 0.1617 | 0.1824 | 100.2693 |
| WAT-1  | ol 4 | c     | 40.07            | 0.0221           | 0.0358                         | 0.0474                         | 12.09 | 0.1051 | 47.54 | 0.1581 | 0.2232 | 100.2917 |
| WAT-1  | ol 5 | c     | 39.26            | 0.0127           | 0.0198                         | 0.0139                         | 17.4  | 0.2833 | 42.81 | 0.1004 | 0.173  | 100.0731 |
| WAT-1  | ol 6 | c     | 39.49            | 0.0542           | 0.0386                         | 0.0614                         | 15.67 | 0.2384 | 44    | 0.1933 | 0.1467 | 99.8926  |
| WAT-1  | ol 5 | I.Z.  | 40.09            | 0.0131           | 0.0573                         | 0.0786                         | 12.7  | 0.1873 | 46.94 | 0.1632 | 0.1849 | 100.4144 |
| WAT-1  | ol 5 | o.Z.  | 39.17            | 0.0129           | 0.0341                         | 0.0143                         | 16.23 | 0.3333 | 44.1  | 0.2959 | 0.1264 | 100.3169 |
| WAT-1  | ol 1 | r     | 39.42            | 0.0211           | 0.0491                         | -                              | 16.26 | 0.268  | 43.52 | 0.3581 | 0.1487 | 100.045  |
| WAT-1  | ol 2 | r     | 39.32            | 0.0399           | 0.0329                         | -                              | 16.47 | 0.3338 | 43.82 | 0.3176 | 0.0439 | 100.3781 |
| WAT-1  | ol 3 | r     | 39.53            | 0.0289           | 0.0262                         | -                              | 15.87 | 0.3728 | 43.78 | 0.4522 | 0.0903 | 100.1504 |
| WAT-1  | ol 4 | r     | 39.41            | 0.0381           | 0.0292                         | 0.024                          | 15.88 | 0.2514 | 44.59 | 0.2595 | 0.1135 | 100.5957 |
| WAT-1  | ol 6 | r     | 39.54            | 0.0488           | 0.0189                         | 0.0101                         | 15.94 | 0.4266 | 43.53 | 0.5221 | 0.0739 | 100.1104 |
| WAT-1  | ol 1 | r 2   | 39.2             | 0.0445           | 0.0269                         | 0.0296                         | 16.62 | 0.3282 | 43.89 | 0.2963 | 0.1464 | 100.5819 |
| DSAT-2 | ol1  | r     | 38.64            | 0.1013           | 0.0144                         | -                              | 17.65 | 0.3629 | 42.81 | 0.47   | 0.0528 | 100.1014 |
| DSAT-2 | ol 1 | c     | 38.6             | 0.0609           | 0.0563                         | 0.0645                         | 19.27 | 0.2346 | 41.62 | 0.2251 | 0.068  | 100.1994 |
| DSAT-2 | ol 2 | r     | 39.38            | 0.089            | 0.0295                         | -                              | 17.71 | 0.3916 | 42.48 | 0.4452 | 0.0832 | 100.6085 |
| DSAT-2 | ol 2 | c     | 38.89            | 0.0593           | 0.0584                         | -                              | 20.08 | 0.4391 | 40.92 | 0.2288 | 0.0725 | 100.7481 |
| DSAT-2 | ol 2 | c 2   | 38.59            | 0.0769           | 0.0257                         | 0.0299                         | 19.94 | 0.4968 | 40.86 | 0.2006 | 0.0606 | 100.2805 |
| DSAT-2 | ol 3 | r     | 39.38            | 0.0576           | 0.0061                         | 0.0152                         | 16.61 | 0.441  | 43.29 | 0.6377 | 0.0645 | 100.5021 |
| DSAT-2 | ol 3 | c     | 39.17            | 0.0334           | 0.0372                         | 0.0281                         | 19.23 | 0.337  | 41.36 | 0.2095 | 0.1206 | 100.5258 |
| DSAT-2 | ol 4 | r     | 39.16            | 0.0421           | 0.0197                         | 0.0416                         | 18.51 | 0.3419 | 42.13 | 0.4103 | 0.0538 | 100.7094 |
| DSAT-2 | ol 4 | r     | 39.13            | 0.0796           | 0.0432                         | 0.0625                         | 19.24 | 0.3636 | 41.38 | 0.328  | 0.0842 | 100.7111 |
| DSAT-2 | ol 4 | c     | 39.17            | 0.0394           | 0.0281                         | -                              | 19.04 | 0.3528 | 41.57 | 0.1824 | 0.0984 | 100.4811 |
| DSAT-2 | ol 5 | r     | 39.05            | 0.113            | 0.0266                         | 0.0045                         | 18.33 | 0.387  | 42.45 | 0.5355 | 0.0169 | 100.9135 |
| DSAT-2 | ol 5 | r 2   | 39.34            | 0.0932           | 0.0318                         | 0.0309                         | 19.22 | 0.4327 | 41.24 | 0.5826 | 0.0192 | 100.9904 |
| DSAT-2 | ol 5 | c     | 38.94            | 0.0802           | 0.0539                         | -                              | 19.03 | 0.3109 | 41.36 | 0.2307 | 0.1094 | 100.1151 |
| DSAT-2 | ol 6 | r     | 39.17            | 0.0964           | 0.057                          | 0.0457                         | 19.31 | 0.3203 | 40.98 | 0.2508 | 0.1    | 100.3302 |
| DSAT-2 | ol 6 | c     | 39.28            | 0.0329           | 0.0469                         | -                              | 19.16 | 0.2974 | 41.14 | 0.2262 | 0.0737 | 100.2571 |

\* r =rim c =core l =inner z =zone o =outer

**Appendix B Table 20: A collection of the results for the Fe-oxide crystals analysed by electron microprobe.**

| Type: | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO   | MnO  | MgO   | NiO    | Total | Type:   | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO  | MnO | MgO | NiO | Total |
|-------|------------------|--------------------------------|--------------------------------|-------|------|-------|--------|-------|---------|------------------|--------------------------------|--------------------------------|------|-----|-----|-----|-------|
| WAT-1 |                  |                                |                                |       |      |       |        |       | DSAT-2  |                  |                                |                                |      |     |     |     |       |
| In/OI | 14.12            | 1.33                           | 9.38                           | 65.80 | 0.93 | 7.43  | 0.0864 | 99.1  | ph      | 22.9             | 4.7                            | 0.3                            | 61.6 | 0.7 | 7.1 | -   | 97.3  |
| ph    | 14.77            | 0.88                           | -                              | 73.97 | 1.02 | 5.94  | 0.0475 | 96.6  | ph      | 23.8             | 4.4                            | 0.2                            | 60.4 | 0.8 | 7.7 | -   | 97.2  |
| FG    | 13.62            | 0.76                           | 4.55                           | 72.20 | 1.16 | 5.48  | 0.0455 | 97.8  | ph      | 19.9             | 5.7                            | 6.3                            | 56.6 | 0.6 | 8.3 | -   | 97.5  |
| FG    | 13.59            | 0.75                           | 4.57                           | 71.26 | 1.18 | 5.51  | 0.0089 | 96.9  | ph      | 21.6             | 5.0                            | 2.0                            | 60.6 | 0.7 | 6.4 | -   | 96.5  |
| FG    | 13.01            | 0.78                           | 5.80                           | 69.55 | 1.19 | 5.48  | 0.0882 | 95.9  | ph      | 18.4             | 5.7                            | 4.1                            | 60.6 | 0.6 | 7.7 | -   | 97.2  |
| FG    | 13.80            | 0.92                           | 2.84                           | 69.47 | 1.15 | 4.92  | 0.0365 | 93.1  | ph      | 22.2             | 4.9                            | 0.7                            | 61.1 | 0.6 | 7.4 | 0.1 | 97.0  |
| ph    | 15.97            | 1.13                           | 0.76                           | 70.74 | 1.18 | 6.25  | 0.0651 | 96.1  | ph      | 19.3             | 5.4                            | 2.1                            | 60.9 | 0.5 | 8.1 | -   | 96.3  |
| ph    | 14.56            | 0.73                           | 2.84                           | 71.27 | 1.15 | 5.34  | 0.0631 | 96.0  | ph      | 22.2             | 4.6                            | 0.1                            | 61.0 | 0.6 | 8.0 | -   | 96.6  |
| ph    | 13.84            | 0.93                           | 0.17                           | 73.28 | 1.04 | 5.89  | -      | 95.2  | ph      | 24.5             | 4.5                            | 0.5                            | 59.9 | 0.8 | 7.5 | -   | 97.7  |
| mg    | 11.79            | 1.20                           | 13.54                          | 65.11 | 1.20 | 6.04  | 0.0133 | 98.9  | ph      | 22.8             | 4.9                            | 0.0                            | 63.2 | 0.9 | 4.6 | -   | 96.4  |
| ph    | 11.13            | 1.60                           | 14.72                          | 63.75 | 1.25 | 6.24  | 0.0599 | 98.8  | ph      | 24.1             | 4.4                            | 0.1                            | 62.6 | 0.9 | 4.7 | -   | 96.7  |
| mg    | 10.23            | 4.08                           | 16.05                          | 60.85 | 1.10 | 7.02  | 0.0622 | 99.4  | ph      | 16.1             | 4.1                            | 2.2                            | 68.8 | 0.7 | 4.5 | -   | 96.5  |
| ph    | 16.08            | 1.21                           | 0.62                           | 70.61 | 1.15 | 6.27  | 0.0465 | 96.0  | ph      | 21.7             | 5.2                            | 0.0                            | 63.9 | 0.9 | 4.9 | -   | 96.7  |
| ph    | 14.71            | 0.72                           | 0.04                           | 72.20 | 1.18 | 5.66  | 0.0684 | 94.6  | ph      | 24.2             | 4.2                            | 0.1                            | 60.4 | 0.8 | 7.0 | -   | 96.7  |
| FG    | 13.99            | 0.71                           | 2.80                           | 70.44 | 1.28 | 5.23  | 0.0044 | 94.5  | ph      | 22.7             | 4.8                            | 0.1                            | 61.7 | 0.9 | 5.8 | -   | 95.9  |
| LOU-3 |                  |                                |                                |       |      |       |        |       | ph      | 22.6             | 4.8                            | 0.1                            | 61.1 | 0.8 | 6.7 | -   | 96.1  |
| ph    | 18.97            | 3.45                           | 0.07                           | 65.43 | 1.64 | 6.39  | 0.0877 | 96.0  | ph      | 24.5             | 4.4                            | 0.0                            | 60.3 | 0.8 | 7.2 | -   | 97.2  |
| ph    | 13.15            | 7.86                           | 9.92                           | 57.25 | 1.00 | 10.13 | 0.1327 | 99.4  | ph      | 24.1             | 4.3                            | 0.0                            | 63.0 | 0.9 | 4.9 | -   | 97.1  |
| ph    | 4.12             | 4.10                           | 0.04                           | 78.83 | 1.01 | 4.13  | 0.0623 | 92.3  | FG      | 26.4             | 3.0                            | 0.0                            | 63.6 | 1.2 | 2.6 | -   | 96.8  |
| ph    | 17.50            | 2.40                           | 0.02                           | 66.98 | 1.66 | 5.53  | 0.0661 | 94.2  | FG      | 26.8             | 2.7                            | 0.0                            | 61.7 | 1.2 | 2.9 | -   | 95.3  |
| ph    | 18.60            | 3.50                           | -                              | 65.78 | 1.61 | 6.26  | 0.0424 | 95.8  | FG      | 27.0             | 2.1                            | 0.0                            | 63.6 | 1.1 | 2.0 | -   | 95.9  |
| ph    | 18.45            | 4.12                           | 0.04                           | 65.50 | 1.57 | 6.21  | 0.0292 | 95.9  | FG      | 25.2             | 3.9                            | 0.0                            | 63.4 | 1.0 | 3.2 | -   | 96.9  |
| ph    | 17.54            | 3.83                           | 0.20                           | 66.86 | 1.70 | 5.81  | 0.004  | 95.9  | BIESE-1 |                  |                                |                                |      |     |     |     |       |
| ph    | 17.75            | 3.75                           | 0.60                           | 65.67 | 1.56 | 6.14  | 0.051  | 95.5  | ph      | 24.0             | 4.2                            | 1.0                            | 59.9 | 0.7 | 7.4 | -   | 97.2  |
| ph    | 15.14            | 1.61                           | 0.15                           | 71.60 | 1.51 | 4.49  | -      | 94.5  | ph      | 24.5             | 4.0                            | 0.1                            | 61.8 | 0.9 | 5.2 | -   | 96.5  |
| ph    | 15.59            | 1.08                           | 0.10                           | 72.05 | 1.49 | 4.45  | 0.0642 | 94.8  | ph      | 23.6             | 4.3                            | 1.6                            | 59.1 | 0.7 | 7.4 | -   | 96.8  |
| ph    | 15.32            | 1.49                           | 0.32                           | 70.98 | 1.60 | 4.49  | 0.0838 | 94.3  | ph      | 24.4             | 4.0                            | 0.5                            | 60.8 | 0.8 | 6.6 | -   | 97.1  |
| ph    | 15.96            | 2.44                           | 0.03                           | 70.12 | 1.61 | 5.21  | -      | 95.4  | ph      | 24.4             | 4.3                            | 1.0                            | 60.3 | 0.8 | 7.4 | -   | 98.1  |
| ph    | 15.83            | 3.14                           | 1.20                           | 68.36 | 1.59 | 5.36  | 0.0698 | 95.6  | ph      | 24.0             | 4.5                            | 0.1                            | 60.3 | 0.8 | 7.4 | -   | 97.0  |
| ph    | 14.97            | 2.27                           | 0.68                           | 70.19 | 1.58 | 4.96  | 0.002  | 94.7  | ph      | 23.9             | 4.4                            | 2.1                            | 61.1 | 0.7 | 7.4 | -   | 99.7  |
| ph    | 11.37            | 5.61                           | 10.35                          | 62.24 | 1.52 | 5.66  | 0.0605 | 96.8  | ph      | 20.5             | 5.4                            | 3.2                            | 60.3 | 0.8 | 7.5 | -   | 97.7  |
| ph    | 18.01            | 3.48                           | 0.06                           | 66.93 | 1.70 | 5.72  | 0.0464 | 95.9  |         |                  |                                |                                |      |     |     |     |       |
| FG    | 14.84            | 0.43                           | 0.12                           | 73.00 | 1.45 | 4.28  | 0.004  | 94.1  |         |                  |                                |                                |      |     |     |     |       |
| FG    | 15.18            | 0.68                           | 0.07                           | 72.33 | 1.51 | 4.40  | 0.0542 | 94.2  |         |                  |                                |                                |      |     |     |     |       |
| FG    | 15.04            | 1.75                           | 0.56                           | 70.54 | 1.51 | 4.79  | 0.0926 | 94.3  |         |                  |                                |                                |      |     |     |     |       |

## 10.3. Appendix C: Petrographic Descriptions

**Appendix C: Table 21: Petrographic description of the melilitite samples collected in this study.**

| Sample           | Description                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                           |
|------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>BIES-10A</b>  | The sample contains slightly altered phenocrysts of olivine (<5 mm to 0.1 mm) and opaque (<2mm to 0.01 mm) minerals in a fine grained matrix. The olivine phenocrysts are variable in shape between euhedral tabular grains, skeletal and irregular fragments. The matrix consists primarily of very fine grained acicular clinopyroxene (<0.2 mm), fine to very fine grained euhedral and subhedral opaque minerals as well as fine grained euhedral perovskite, interstitial nepheline and glass.                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
| <b>BIES-11A</b>  | The sample contains euhedral and skeletal shaped phenocrysts of olivine (<3 to 0.1 mm) as well as fine grained olivine fragments. The olivine grains are altered along their edges or completely altered for some smaller grains into clay minerals. The sample also contains angular to subhedral phenocrysts of opaque minerals (<2 mm to 0.01 mm) and very fine grained opaque mineral grains in the matrix. The matrix consists mostly of very fine grained short clinopyroxene (<0.2 mm) needles as well as angular grains of fine grained perovskite (~0.1 mm) and scatted areas of interstitial nepheline.                                                                                                                                                                                                                                                                                                                                     |
| <b>BIESA-1</b>   | Partially altered porphyritic olivine nephelinite containing olivine xenocrysts (<5mm diameter) and phenocrysts (5 to 0.1 mm) of altered hopper olivine phenocrysts, skeletal olivine phenocrysts and fine grained fragments. The sample contains a few <1mm diameter opaque mineral phenocrysts and has a fine grained acicular matrix. The matrix consists of abundant very fine grained clinopyroxene needles (<0.1 mm diameter) as well as microphenocrysts of cubic to subhedral perovskite (<0.05 mm diameter) and microphenocrysts of euhedral to subhedral opaque minerals (0.5 to 0.1 mm) as well as abundant fine grained interstitial nepheline, and very fine grained opaque minerals.                                                                                                                                                                                                                                                    |
| <b>BIESA-2</b>   | Partially altered porphyritic olivine nephelinite containing olivine xenocrysts (<5mm diameter) and phenocrysts (5 to 0.1 mm) of altered hopper olivine phenocrysts, skeletal olivine phenocrysts and fine grained fragments. The sample contains a few <1mm diameter opaque mineral phenocrysts and has a fine grained acicular matrix. The matrix consists of abundant very fine grained clinopyroxene needles (<0.1 mm diameter) as well as microphenocrysts of cubic to subhedral perovskite (<0.05 mm diameter) and microphenocrysts of euhedral to subhedral opaque minerals (0.5 to 0.1 mm) as well as abundant fine grained interstitial nepheline, and very fine grained opaque minerals.                                                                                                                                                                                                                                                    |
| <b>BIESA-VM1</b> | Pervasive alteration of olivine phenocrysts to clay minerals as well as alteration of opaque minerals to finer grained clay and secondary minerals. Significant number of vesicles filled with zeolites and clay minerals. Alignment of the vesicles suggesting they aligned during slow movement of magma. Matrix of a fine grained acicular nature containing very fine grained needles of altered clinopyroxene, microphenocrysts of partially altered perovskite, and microphenocrysts of relatively fresh to subhedral opaque minerals. The sample also contains partially altered interstitial nepheline and phlogopite.                                                                                                                                                                                                                                                                                                                        |
| <b>BIESB-1</b>   | The sample contains mostly fresh phenocrysts of euhedral, skeletal and hopper olivine grains and fine fragments of a variable grain size (3 to 0.1 mm diameter) as well as medium grained opaque mineral phenocrysts (<1 mm diameter) surrounded by a matrix of fine to very fine subhedral opaque mineral microphenocrysts (<0.1 mm), subhedral to cubic perovskite microphenocrysts (~0.1 mm), very fine grained clinopyroxene needles (<0.2 mm) and tabular melilitite (<0.2 mm). The matrix also contains fine grained anhedral/interstitial microcrystalline nepheline and fine grained glass.                                                                                                                                                                                                                                                                                                                                                   |
| <b>BIESB-2</b>   | The sample contains mostly fresh phenocrysts of euhedral, skeletal and hopper olivine of a variable grain-size (4 to 0.1 mm diameter) as well as medium grained opaque mineral phenocrysts (<0.5 mm) surrounded by a matrix of fine to very fine subhedral opaque mineral microphenocrysts (<0.1 mm), subhedral to cubic perovskite microphenocrysts (~0.1 mm), very fine grained clinopyroxene needles (<0.2 mm) and tabular melilitite (<0.2 mm). The matrix also contains fine grained anhedral/interstitial microcrystalline nepheline and fine grained glass. The sample has a low degree of alteration where clay minerals are present in the matrix with alteration of melilitite. Some alteration of olivine grains has occurred along fractures and grain boundaries.                                                                                                                                                                        |
| <b>BIESB-3</b>   | The sample contains mostly fresh phenocrysts of euhedral, skeletal and hopper olivine of a variable grain-size (3 to 0.1 mm diameter) as well as medium grained opaque mineral phenocrysts (<1 mm) surrounded by a matrix of fine to very fine subhedral opaque mineral microphenocrysts (<0.1 mm), subhedral to cubic perovskite microphenocrysts (~0.1 mm), very fine grained clinopyroxene needles (<0.2 mm) and tabular melilitite (<0.2 mm). The matrix also contains fine grained anhedral/interstitial microcrystalline nepheline and fine grained glass.                                                                                                                                                                                                                                                                                                                                                                                      |
| <b>BIESC-1</b>   | Coarse grained porphyritic olivine melilitite with abundant olivine phenocrysts as well as a few phenocrysts of opaque minerals in a fine grained matrix. Olivine occurs as fresh phenocrysts of various shapes including skeletal, hopper and euhedral tabular shaped grains as well as fine grained fragments. The groundmass appears to be fresh and consists of angular subhedral opaque mineral phenocrysts, very fine grained opaque minerals, microphenocrysts of perovskite and randomly oriented tabular microphenocrysts of melilitite. The groundmass minerals show an apparent flow texture which suggests the movement of magmatic material during crystallization. The sample shows variation in groundmass textures suggesting areas of differing grain-size, mineral abundance and composition on a thin section scale. Trace amounts of CPX and nepheline are present.                                                               |
| <b>BIESC-2</b>   | Relatively coarse grained densely packed porphyritic olivine melilitite with areas of differing composition. Areas appear to have undergone mixing of different composition with physical flow between areas. Olivine is the predominant phenocryst. The sample has a few irregular phenocrysts of opaque phases. The groundmass contains an inter-grown assemblage of abundant opaque mineral microphenocrysts as well as very fine grained opaque mineral grains, variably distributed perovskite microphenocrysts, melilitite microphenocrysts, clinopyroxene microphenocrysts and interstitial nepheline. The sample has areas of differing mineralogical composition suggesting the flow of different magma compositions during mixing. Alteration in the sample is sporadic with patches of alteration visible mostly in the groundmass.                                                                                                        |
| <b>BIESC-3</b>   | The sample is a fresh porphyritic olivine melilitite with slightly variable composition suggesting mixing of variable magma types. Abundant olivine phenocrysts of variable shape and sizes from 5 mm long tabular grains too <2mm wide skeletal grains as well as <1 mm wide euhedral grains as well as fine grained fragments in up to ground mass size. Few <1mm phenocrysts of opaque minerals as well as abundant microphenocrysts of opaque minerals and a very fine grained opaque mineral. The sample contains microphenocrysts of tabular melilitite and cubic perovskite also present. A very fine grained indistinguishable groundmass phase or glass is also present.                                                                                                                                                                                                                                                                     |
| <b>BIESD-1</b>   | Partially altered medium grained olivine clinopyroxene nephelinite with fine grained inter-grown clinopyroxene and alteration mineral groundmass. Less than 5mm tabular olivine grains as well as more abundant <0.5 mm euhedral olivine grains and fine grained olivine fragments. Few fine grained opaque mineral phenocrysts as well as abundant subhedral to euhedral opaque mineral phenocrysts as well as very fine-grained crystals in groundmass. The sample contains few fine grained subhedral perovskite grains as well as abundant interstitial nepheline.                                                                                                                                                                                                                                                                                                                                                                                |
| <b>BIESD-2</b>   | The sample consists of fresh olivine phenocrysts and fragments surrounded by a groundmass of intergrown acicular clinopyroxene, interstitial nepheline, opaque mineral microphenocrysts and perovskite microphenocrysts. The samples has mostly medium grained <1mm olivine phenocrysts of a euhedral shape. There are a few skeletal olivine grains and olivine megacrysts. Abundant cubic and angular microphenocrysts of opaque minerals as well as very fine grained opaque mineral grains in ground mass. The sample has abundant cubic perovskite grains. Intergrown tabular grains of clinopyroxene and tabular melilitite occur as the main ground mass phase. Contains amygdales filled with unknown alteration phase.                                                                                                                                                                                                                       |
| <b>BIESD-3</b>   | The sample is extensively but not pervasively altered fine grained olivine nephelinite with fine grained inter-grown groundmass of acicular clinopyroxene, subhedral perovskite microphenocrysts, interstitial nepheline and fine to very fine grained opaque mineral microphenocrysts. Amygdales filled with zeolites and clay minerals.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| <b>BIESD-4</b>   | Pervasively altered fine grained olivine melilitite containing olivine phenocrysts, a few phenocrysts of opaque minerals and amygdales. These are surrounded by a groundmass of fine grained intergrown tabular needles of mainly clinopyroxene, abundant cubic microphenocrysts of perovskite, angular microphenocrysts of opaque minerals, minor irregular nepheline grains and minor tabular microphenocrysts of melilitite. The groundmass also contains a fine grained dusting of opaque minerals. The olivine grains are mostly <2mm in size and vary in shape between tabular to euhedral in shape with alteration along fractures and grain boundaries. The opaque mineral phenocrysts are irregular in shape and contain resorption cavities. The amygdales vary in size from 5 mm to 0.5 mm in diameter. They appear to be filled with clinopyroxene needles of various length and fine grained zeolites or radiating monticellite needles. |

## Appendix C: Table 21 continued: Petrographic description of the melilitite samples collected in this study.

| Sample          | Description                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
|-----------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| <b>BIESE-1</b>  | The sample is a medium grained, partially altered porphyritic nephelinite with a coarse grained groundmass of intergrown needlesh of clinopyroxene, opaque minerals, perovskite and nepheline. The sample contains a few <2 mm skeletal and tabular phenocrysts of olivine as well as few euhedral olivine phenocrysts. Olivine altered along grain boundaries to clay minerals. Abundant fine grained <1 mm opaque mineral phenocrysts and microphenocrysts as well as very fine grained groundmass dusting. The sample contains minor fresh microphenocrysts of cubic perovskite. Perovskite occurs as relatively coarse grained microphenocrysts with opaque mineral microphenocrysts and inter-grown needle like clinopyroxene and interstitial nepheline.                                                                                                                                                          |
| <b>BIESE-2</b>  | The sample contains slightly altered medium grained olivine melilitite with medium grained inter-grown matrix of clinopyroxene needles, as well as abundant subhedral to cubic phenocrysts of opaque minerals, cubic to subhedral perovskite (<0.1mm) and interstitial nepheline. The sample contains minor tabular <5 mm long olivine phenocrysts, abundant <1 mm euhedral olivine phenocrysts and fine olivine fragments. Abundant <1 mm opaque mineral phases as well as abundant opaque mineral microphenocrysts and fine ground mass dusting.                                                                                                                                                                                                                                                                                                                                                                      |
| <b>BIESE-3</b>  | Partially altered olivine clinopyroxene nephelinite with medium grained intergrown groundmass of fine grained opaque minerals, clinopyroxene and interstitial nepheline. Mostly medium grained (<1mm) euhedral and skeletal olivine phenocrysts as well as fine fragments that have all been altered along grain boundaries to clay minerals. The sample contains abundant very fine to medium grained irregular and angular microphenocrysts and phenocrysts of opaque minerals. The sample contains minor cubic perovskite as well as abundant inter-cumulus nepheline.                                                                                                                                                                                                                                                                                                                                               |
| <b>DIK-10 A</b> | Fresh porphyritic olivine melilitite with coarse grained olivine phenocrysts and opaque mineral phenocrysts supported by a very fine grained groundmass containing mostly glass, minor amounts of very fine grained tabular melilitite (<0.1 mm), abundant microphenocrysts of cubic perovskite (<0.2 mm), as well as fine grained angular or cubic opaque mineral microphenocrysts (<0.5 mm) and very fine grained dust sized particles (<0.01 mm). The sample contains a few coarse grained angular phenocrysts of opaque minerals (<5 mm diameter). Tabular skeletal <5 mm and hopper olivines of <1 mm as well as <1 mm euhedral olivines. The sample has numerous fine grained fragments of olivine. The sample has fine interstitial nepheline. Olivine megacrysts with stress bands visible in cross polarized light. The sample contains areas which appear to have very fine grained needles of clinopyroxene. |
| <b>DIK-10 B</b> | The sample contains fresh coarse grained porphyritic olivine melilitite containing fine grained groundmass of abundant microphenocrysts of opaque minerals as well as very fine grained opaque minerals, minor tabular melilitite phenocrysts and euhedral microphenocrysts of perovskite. The sample contains variably shaped and sized olivine phenocrysts with some euhedral olivine phenocrysts as well as microphenocrysts and fragments of olivine. The sample also contains macrocrysts of olivine which has deformational lamellae that are visible on extinction. The sample contains trace amounts of extremely fine grained needle shaped clinopyroxene needles as a groundmass phase.                                                                                                                                                                                                                       |
| <b>DIK-11 A</b> | The sample contains fresh coarse grained porphyritic olivine melilitite with a fine grained ground mass consisting mainly of microphenocrysts of opaque minerals as well as very fine grained opaque mineral grains. The groundmass also contains trace amounts of tabular melilite and abundant very fine grained needles of clinopyroxene which appear to replace to melilite. Abundant perovskite is present as microphenocrysts. Olivine occurs as variable shaped phenocrysts commonly containing inclusions of opaque minerals within some grains and concentrated at the margins of other grains. Tabular and euhedral olivine grains are present with grain size between 2mm and very fine grained fragments.                                                                                                                                                                                                   |
| <b>DIK-11 B</b> | Fresh coarse grained porphyritic olivine melilitite with a fine grained groundmass consisting mainly of microphenocrysts of opaque minerals as well as very fine grained opaque mineral grains. The groundmass also contains trace amounts of tabular melilite and abundant very fine grained needles of clinopyroxene which appear to replace to melilite. Abundant perovskite is present as microphenocrysts. Olivine occurs as variable shaped phenocrysts commonly containing inclusions of opaque minerals within some grains and concentrated at the margins of other grains. Tabular and euhedral olivine grains are present with grain size between 2mm and very fine grained fragments.                                                                                                                                                                                                                        |
| <b>DIK-12-A</b> | Fresh coarse grained porphyritic olivine melilitite with a very fine grained groundmass consisting mainly of microphenocrysts of opaque minerals, microphenocrysts of perovskite, lesser tabular melilitite, abundant fine grained intercumulus nepheline, fine fragments of olivine and very fine grained opaque minerals. Minor <1mm phenocrysts of opaque minerals are present as well as abundant phenocrysts of olivine <2mm diameter.                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| <b>DIK-12-B</b> | Fresh coarse grained porphyritic olivine melilitite with a very fine grained groundmass consisting mainly of microphenocrysts of opaque minerals, microphenocrysts of perovskite, lesser tabular melilitite, abundant fine grained intercumulus nepheline, fine fragments of olivine and very fine grained opaque minerals. Minor <1mm phenocrysts of opaque minerals are present as well as abundant phenocrysts of olivine <2mm diameter.                                                                                                                                                                                                                                                                                                                                                                                                                                                                             |
| <b>DIK-13</b>   | Fresh coarse grained porphyritic olivine melilitite with a very fine grained groundmass consisting mainly of microphenocrysts of opaque minerals, microphenocrysts of perovskite, lesser tabular melilitite, abundant fine grained intercumulus nepheline, fine fragments of olivine and very fine grained opaque minerals. Minor <1mm phenocrysts of opaque minerals are present as well as abundant phenocrysts of olivine <2mm diameter. Hourglass shaped melilitite laths.                                                                                                                                                                                                                                                                                                                                                                                                                                          |
| <b>DIK-VM1</b>  | The sample consists of an altered medium grained matrix which surrounds phenocrysts of olivine (<2 to 0.5 mm diameter) and amygdaloids (<5 mm to 0.5 mm diameter) filled with zeolites. The olivine phenocrysts are relatively fresh with only slight alteration on their margins and in fractures and they vary in shape between euhedral grains and medium to fine grained fragments. The matrix consists of fine grained glass and clay minerals forming areas between grains of pervasively altered tabular melilite (<1 to 0.5 mm) which has been altered to fine grained green to honey brown clays. The matrix also contains subhedral angular opaque mineral grains (<1.0 to 0.01 mm), angular euhedral perovskite (0.1 mm) and fine grained tabular to needle like clinopyroxene (<0.5 to 0.01 mm length). Trace amounts of fine grained nepheline occur as interstitial phase.                                |
| <b>DIK-VM2</b>  | The sample consists of an altered medium grained matrix which surrounds phenocrysts of olivine (<2 to 0.5 mm diameter) and amygdaloids (<1 mm to 0.5 mm diameter) filled with zeolites. The olivine phenocrysts are partially altered with alteration on their margins and in fractures and they vary in shape between euhedral grains and medium to fine grained fragments. The matrix consists of fine grained glass and clay minerals forming areas between remnant grains of pervasively altered tabular melilite (<1 to 0.5 mm) which has been almost completely altered to fine grained green to light brown clays. The matrix also contains subhedral angular opaque mineral grains (<1.0 to 0.01 mm), angular euhedral perovskite (0.1 mm) and fine grained tabular to needle like clinopyroxene (<0.5 to 0.01 mm length). The sample contains irregular fine grained nepheline.                                |
| <b>DIK-VM3</b>  | The sample contains medium grained euhedral and skeletal phenocrysts as well as microphenocrysts and fragments of olivine (<4 by 0.1 mm) which are aligned along their C axis to create a foliation. The sample also contains a few amygdaloids (<0.1 mm) containing fine grained clays. The matrix consists of rounded areas of fine grained crystals and glass, as well as remnant tabular crystals of melilite (<0.5 to 0.1 mm length) which have been pervasively altered and replaced by clay minerals. The matrix contains abundant fine grained needles of clinopyroxene (0.5 to 0.1 mm length), abundant subhedral to euhedral opaque minerals (<0.5 to 0.01 mm), minor euhedral perovskite (0.2 to 0.1 mm) and very fine grained interstitial nepheline.                                                                                                                                                       |
| <b>DIK-VM4</b>  | The sample consists of an altered medium grained matrix which surrounds phenocrysts of olivine (<2 to 0.5 mm diameter) and amygdaloids (<1 mm to 0.5 mm diameter) filled with zeolites. The olivine phenocrysts are partially altered with alteration on their margins and in fractures and they vary in shape between euhedral grains and medium to fine grained fragments. The matrix consists of fine grained glass and clay minerals forming areas between remnant grains of pervasively altered tabular melilite (<1 to 0.5 mm) which has been almost completely altered to fine grained green to light brown clays. The matrix also contains subhedral angular opaque mineral grains (<1.0 to 0.01 mm), angular euhedral perovskite (0.1 mm) and fine grained tabular to needle like clinopyroxene (<0.5 to 0.01 mm length). The sample contains irregular fine grained nepheline.                                |
| <b>DIK-VM3</b>  | The sample contains medium grained euhedral and skeletal phenocrysts as well as microphenocrysts and fragments of olivine (<4 by 0.1 mm) which are aligned along their C axis to create a foliation. The sample also contains a few amygdaloids (<0.1 mm) containing fine grained clays. The matrix consists of rounded areas of fine grained crystals and glass, as well as remnant tabular crystals of melilite (<0.5 to 0.1 mm length) which have been pervasively altered and replaced by clay minerals. The matrix contains abundant fine grained needles of clinopyroxene (0.5 to 0.1 mm length), abundant subhedral to euhedral opaque minerals (<0.5 to 0.01 mm), minor euhedral perovskite (0.2 to 0.1 mm) and very fine grained interstitial nepheline.                                                                                                                                                       |

## Appendix C: Table 21 continued: Petrographic description of the melilitite samples collected in this study.

| Sample  | Description                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                               |
|---------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| DIK-VM4 | The sample consists of an altered medium grained matrix which surrounds phenocrysts of olivine (<2 to 0.5 mm diameter) and amygdales (<1 mm to 0.5 mm diameter) filled with zeolites. The olivine phenocrysts are partially altered with alteration on their margins and in fractures and they vary in shape between euhedral grains and medium to fine grained fragments. The matrix consists of fine grained glass and clay minerals forming areas between remnant grains of pervasively altered tabular melilite (<1 to 0.5 mm) which has been almost completely altered to fine grained green to light brown clays. The matrix also contains subhedral angular opaque mineral grains (<1.0 to 0.01 mm), angular euhedral perovskite (0.1 mm) and fine grained tabular to needle like clinopyroxene (<0.5 to 0.01 mm length). The sample contains irregular fine grained nepheline.                                                                                                                                                                                                                                                                                    |
| DSAT-1  | The sample contains fresh, fine grained acicular nepheline with a few euhedral olivine phenocrysts as well as olivine microphenocrysts and very fine-grained fragments (3 mm to 0.2 mm). The main mineral constituent is acicular clinopyroxene which forms 0.5 to 0.01 mm long needles by 0.02 width of an intergrown and slightly aligned nature. The sample also contains abundant anhedral to subhedral opaque mineral microphenocrysts (0.5 to 0.1 mm) and abundant cubic to angular very fine grained crystals (0.02 to 0.01 mm) of opaque minerals. This sample contains no visible melilite. The sample contains a few angular to cubic microphenocrysts of perovskite (0.3 to 0.1 mm). Irregular interstitial oikocrysts of nepheline surrounding clinopyroxene needles as well as finer grained crystals (0.5 to 0.02 mm). Very slight alteration is present in the groundmass as green areas in plane polarized light which appear isotropic in cross polarized light.                                                                                                                                                                                         |
| DSAT-2  | The sample contains predominantly intergrown randomly oriented clinopyroxene which forms elongate; needles of between ~1.0 to 0.2 mm long which varies in thickness between 0.3 and 0.1 mm. The clinopyroxene forms a groundmass phase along with opaque minerals forming microphenocrysts of ~0.5 mm to 0.01 mm diameter, as well as olivine fragments, very few grains of melilite, intercumulus nepheline, and abundant sodalite forming a microphenocrysts phase of ~0.5 to 0.02 mm diameter subhedral grains. A few cubic microphenocrysts of perovskite are disseminated across the groundmass (0.1 mm diameter). The main phenocrysts phase is olivine (2 mm diameter or less) which shows a slight orientation by alignment of the length of grains in a common direction. The olivine appears to be relatively fresh with only slight alteration along grain margins. The olivine grains appear to contain inclusions of an early melt phase. The groundmass minerals are altered across the sample to form a slight green to brown discoloration in transmitted light and patches of fine grained clay minerals are visible within the fine grained groundmass. |
| DSAT-3A | The sample contains predominantly intergrown randomly oriented clinopyroxene which forms tabular and elongate needle like crystals of between ~1.0 to 0.2 mm long which vary thickness between 0.3 and 0.1 mm. The clinopyroxene forms a groundmass phase along with opaque minerals forming microphenocrysts of ~0.5 mm to 0.01 mm diameter, as well as olivine fragments, very few grains of melilite, intercumulus nepheline, and abundant sodalite forming a microphenocrysts phase of ~0.5 to 0.02 mm diameter subhedral grains. A few cubic microphenocrysts of perovskite are disseminated across the groundmass (0.1 mm diameter). The main phenocrysts phase is olivine (2 mm diameter or less) which shows a slight orientation by alignment of the length of grains in a common direction. The olivine appears to be relatively fresh with only slight alteration along grain margins. The olivine grains appear to contain inclusions of an early melt phase.                                                                                                                                                                                                 |
| DSAT-3B | Fresh fine grained acicular clinopyroxene olivine nepheline containing a groundmass of acicular clinopyroxene intergrown microphenocrysts of opaque minerals, sodalite, subhedral perovskite, olivine fragments interstitial nepheline which together surround phenocrysts of olivine and opaque minerals. The olivine grains are variable in size (between 5 mm length and 2 mm down to 0.1 mm size fragments) and are generally subhedral to euhedral in shape with inclusions of unknown fine grained brown mineral phase. The opaque minerals are <1 mm in diameter and form clusters of euhedral and subhedral grains as well as very fine grained <0.01 mm variably shaped grains. Clinopyroxene forms the majority of the sample and occurs as elongate needles and shorter tabular crystals which are intergrown with the fine grained opaque minerals as well as the interstitial nepheline. The sodalite forms irregular microphenocrysts. Perovskite is randomly disseminated in the sample as irregular subhedral to euhedral grains of 0.2 to 0.05 mm diameter.                                                                                              |
| DSAT-4  | Sample DSAT-4 contains a groundmass of fine grained tabular clinopyroxene and lesser tabular clinopyroxene which is the predominant mineral that is intergrown with fine grained opaque minerals that vary between 1 mm to 0.5 mm diameter angular microphenocrysts as well as very fine grained crystals <0.01 mm. The other groundmass minerals include minor interstitial nepheline, minor subhedral perovskite microphenocrysts 0.2 to 0.1 mm diameter and angular fragments of olivine. Slight alteration of the groundmass clinopyroxene is present in areas. Sodalite occurs in trace amounts as a groundmass phase. The sample contains subhedral to euhedral phenocryst (3mm to 0.5 mm diameter) of olivine which contains inclusions of opaque minerals as well as fine grained clay minerals.                                                                                                                                                                                                                                                                                                                                                                  |
| LOU-2   | Fresh medium grained porphyritic olivine melilitite containing olivine phenocrysts (<5 mm to 0.5 mm diameter) surrounded by a matrix containing microphenocrysts of tabular melilite (0.5 to 0.1 mm long), cubic and angular opaque minerals (<1 mm to 0.2 mm), cubic to subhedral perovskite (0.1 mm diameter) and very fine grained acicular clinopyroxene (<0.01 mm) and very fine opaque minerals, fine grained interstitial nepheline and glass. It appears that the clinopyroxene is the last phase to form and melilite is relatively coarse grained vs other samples. The sample is slightly altered with clays in the matrix.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                    |
| LOU-3   | The sample contains abundant euhedral to subhedral phenocrysts of olivine (3 to 0.2 mm diameter) as well few phenocrysts of opaque minerals (~1mm diameter). The groundmass consists of microphenocrysts and angular fragments of olivine, abundant tabular microphenocrysts of melilite (0.3 to 0.1 mm), abundant microphenocrysts and very fine opaque mineral grains (<0.1 mm), cubic microphenocrysts of perovskite (0.1 to 0.05 mm). Abundant glass with very fine grained opaque minerals visible.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  |
| LOU-4   | Coarse grained euhedral, tabular and skeletal phenocrysts of olivine (<5 tp 0.5 mm) and subhedral phenocrysts of opaque minerals (<2mm), surrounded by much finer groundmass containing microphenocrysts of olivine and olivine fragments, microphenocrysts of opaque minerals (1 to 0.5 mm), tabular melilite microphenocrysts (mm), cubic perovskite (0.5 to 0.2 mm) phenocrysts and a very fine groundmass of acicular clinopyroxene (<0.2 mm), very fine interstitial nepheline, very fine opaque minerals and glass.                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                 |
| WAT-1   | This partially altered rock has a moderately sorted, dense collection of predominantly olivine phenocrysts of euhedral, tabular, skeletal and possibly xenocrystic shape which vary in size from 5 mm to 0.1 mm in diameter. There are a few phenocrysts of opaque minerals of less than 1 mm diameter. The groundmass is very fine grained and consists mostly of microphenocrysts of opaque minerals down to very fine grains. There are also very fine grained needles and tabular grains of melilite which from 0.5 to 0.02 mm long needles by 0.02 mm diameter. The size of the melilite needles varies across the sample. Some areas have experienced more alteration than others. The groundmass is mostly fine grained clays, glass and very fine opaque minerals. The sample contains trace amounts of fine grained perovskite that is partially altered.                                                                                                                                                                                                                                                                                                        |
| WAT-2   | The sample is a coarse to medium grained olivine melilitite with densely packed phenocrysts and xenocrysts of olivine with poor sorting with olivine grain size variation between 5 mm and 0.2 mm. The sample has abundant micro phenocrysts of olivine as well as fragments of olivine. Microphenocrysts of opaque minerals are abundant with most <0.1 mm, however, a few of 1 mm to 0.2 mm are present. The sample contains abundant tabular microphenocrysts of melilite which is less than 0.2 mm in length. Very fine grained euhedral grains of opaque minerals are found throughout the sample and minor amounts of perovskite occurs as fine grained altered euhedral grains. The predominant phases are a fine grained clay and glass in the matrix. An autolith with the composition similar in appearance to the WAT-1 olivine melilitite sample was also found in WAT-2.                                                                                                                                                                                                                                                                                     |

## 10.4. Appendix D: Major Element Compositions of Whole Rock Samples:

**Appendix D Table 22: Major and trace element data for the whole rock samples from Namaqualand obtained by XRF.**

| Sample:                        | BIES-10 | BIES-11 | BIESA-1 | BIESA-1 Rep 1 | BIESA-2 | BIESA-VM1 | BIESA-CR1 | BIESB-1 | BIESB-2 | BIESB-3 | BIESC-1 | BIESC-2 | BIESC-3 |
|--------------------------------|---------|---------|---------|---------------|---------|-----------|-----------|---------|---------|---------|---------|---------|---------|
| SiO <sub>2</sub>               | 32.29   | 32.36   | 32.08   | 32.49         | 32.14   | 34.26     | 75.20     | 32.48   | 32.79   | 32.19   | 33.45   | 32.37   | 32.95   |
| TiO <sub>2</sub>               | 7.11    | 7.08    | 7.37    | 7.37          | 7.07    | 7.25      | 0.21      | 5.80    | 5.91    | 5.82    | 5.08    | 5.40    | 5.05    |
| Al <sub>2</sub> O <sub>3</sub> | 6.35    | 6.41    | 6.20    | 6.38          | 6.37    | 7.03      | 11.41     | 5.95    | 6.09    | 5.97    | 6.74    | 7.01    | 6.61    |
| Fe <sub>2</sub> O <sub>3</sub> | 20.19   | 20.03   | 20.57   | 20.58         | 20.19   | 18.94     | 1.71      | 18.20   | 17.99   | 18.14   | 18.76   | 19.13   | 18.92   |
| MnO                            | 0.24    | 0.24    | 0.24    | 0.24          | 0.24    | 0.21      | 0.02      | 0.23    | 0.22    | 0.24    | 0.30    | 0.31    | 0.30    |
| MgO                            | 12.16   | 12.17   | 12.63   | 12.71         | 12.27   | 8.10      | 0.07      | 14.68   | 14.25   | 14.45   | 13.52   | 12.59   | 13.66   |
| CaO                            | 12.19   | 11.94   | 12.25   | 12.31         | 12.00   | 12.80     | 0.13      | 14.84   | 13.83   | 15.14   | 14.26   | 14.83   | 14.28   |
| Na <sub>2</sub> O              | 0.94    | 1.11    | 0.84    | 0.83          | 0.97    | 0.44      | 2.07      | 1.20    | 1.16    | 1.18    | 2.58    | 2.54    | 2.23    |
| K <sub>2</sub> O               | 2.11    | 2.38    | 3.01    | 3.08          | 2.39    | 2.29      | 6.74      | 3.02    | 2.05    | 2.67    | 1.93    | 1.91    | 1.51    |
| P <sub>2</sub> O <sub>5</sub>  | 1.34    | 1.34    | 1.40    | 1.40          | 1.35    | 1.48      | 0.01      | 2.00    | 1.94    | 2.08    | 1.68    | 1.83    | 1.70    |
| SO <sub>3</sub>                | 0.06    | 0.08    | 0.04    | 0.04          | 0.07    | b.d.      | b.d.      | 0.06    | 0.08    | 0.12    | 0.03    | 0.08    | 0.03    |
| Cr <sub>2</sub> O <sub>3</sub> | 0.06    | 0.06    | 0.07    | 0.07          | 0.06    | 0.05      | b.d.      | 0.08    | 0.09    | 0.08    | 0.06    | 0.06    | 0.06    |
| NiO                            | 0.03    | 0.03    | 0.04    | 0.04          | 0.03    | 0.03      | 0.01      | 0.04    | 0.04    | 0.04    | 0.03    | 0.03    | 0.03    |
| H <sub>2</sub> O               | 0.59    | 0.83    | 0.44    | 0.32          | 0.71    | 1.06      | 0.26      | 0.22    | 0.40    | 0.26    | 0.07    | 0.29    | 0.20    |
| LOI                            | 2.98    | 2.87    | 1.98    | 1.84          | 2.83    | 5.07      | 0.63      | 0.38    | 2.09    | 0.81    | 0.15    | 0.57    | 0.67    |
| Sum                            | 98.64   | 98.93   | 99.14   | 99.68         | 98.70   | 99.02     | 98.46     | 99.21   | 98.93   | 99.19   | 98.65   | 98.94   | 98.19   |
| Zn                             | 151     | 154     | 156     | 153           | 155     | 142       | 76        | 134     | 131     | 136     | 156     | 165     | 158     |
| Cu                             | 71      | 69      | 71      | 69            | 72      | 64        | <5        | 60      | 60      | 60      | 58      | 62      | 57      |
| Ni                             | 244     | 246     | 271     | 268           | 258     | 245       | <5        | 336     | 318     | 330     | 208     | 180     | 213     |
| Co                             | 117     | 113     | 124     | 120           | 117     | 120       | <5        | 111     | 112     | 111     | 100     | 98      | 103     |
| Mn                             | 2117    | 2144    | 2160    | 2157          | 2166    | 1869      | 128       | 2050    | 2018    | 2055    | 2558    | 2703    | 2636    |
| Cr                             | 420     | 428     | 474     | 477           | 445     | 334       | 25        | 581     | 648     | 581     | 429     | 437     | 422     |
| V                              | 388     | 376     | 394     | 401           | 380     | 408       | 6         | 354     | 355     | 350     | 283     | 316     | 290     |
| Mo                             | <5      | <5      | <5      | <5            | <5      | <5        | 7         | <5      | <5      | <5      | <5      | <5      | <5      |
| Nb                             | 207     | 205     | 208     | 206           | 206     | 204       | 56        | 190     | 181     | 197     | 251     | 272     | 257     |
| Zr                             | 726     | 722     | 638     | 628           | 719     | 779       | 416       | 712     | 678     | 732     | 788     | 892     | 792     |
| Y                              | 28      | 26      | 25      | 21            | 23      | 13        | 120       | 22      | 27      | 29      | 35      | 29      | 37      |
| Sr                             | 1296    | 1179    | 1172    | 1179          | 1197    | 1344      | 29        | 1640    | 1359    | 1725    | 1973    | 2112    | 2053    |
| Rb                             | 124     | 137     | 160     | 163           | 133     | 137       | 346       | 109     | 100     | 82      | 53      | 51      | 37      |
| U                              | 11      | 9       | 9       | 8             | 10      | 12        | <5        | 19      | 15      | 22      | 19      | 22      | 20      |
| Th                             | <5      | <5      | <5      | 5             | 5       | <5        | 40        | <5      | <5      | <5      | <5      | <5      | <5      |
| Pb                             | <5      | <5      | <5      | <5            | <5      | <5        | 29        | <5      | <5      | <5      | <5      | <5      | <5      |
| S                              | 1545    | 1466    | 1329    | 1371          | 1218    | 161       | 197       | 666     | 1012    | 990     | 231     | 703     | 297     |
| Sc                             | 25      | 24      | 26      | 24            | 25      | 22        | <10       | 25      | 23      | 22      | 29      | 28      | 28      |
| Ba                             | 1593    | 1388    | 1131    | 1172          | 1422    | 1628      | 279       | 687     | 1050    | 901     | 665     | 788     | 681     |

*The major oxide results are given in weight percentage and the trace element data are provided in parts per million by weight. The H<sub>2</sub>O content is calculated as the weight % lost upon heating to 110°C for 8 hours, while LOI is calculated as the weight % lost upon heating to 850 °C for 4 hours. "-" indicates that the samples was not analyzed for this element and >5 indicates that the amount detected was less than 5 ppm.*

Appendix D Table 22 Continued:

| Sample<br>:                    | BIESD<br>-1 | BIESD<br>-2 | BIESD<br>-3 | BIESD<br>-4 | BIESD<br>-CR1 | BIESD<br>-CR2 | BIESE<br>-1 | BIESE<br>-2 | BIESE<br>-3 | WAT<br>-1 | WAT<br>-2 | WAT<br>CR1 | WAT<br>CR2 |
|--------------------------------|-------------|-------------|-------------|-------------|---------------|---------------|-------------|-------------|-------------|-----------|-----------|------------|------------|
| SiO <sub>2</sub>               | 31.59       | 31.47       | 31.83       | 31.44       | 74.80         | 75.35         | 32.37       | 31.83       | 32.92       | 36.43     | 35.51     | 75.9<br>9  | 49.3<br>5  |
| TiO <sub>2</sub>               | 7.56        | 7.59        | 7.82        | 7.56        | 0.19          | 0.19          | 7.96        | 7.77        | 7.60        | 4.19      | 4.15      | 0.08       | 0.99       |
| Al <sub>2</sub> O <sub>3</sub> | 7.27        | 7.32        | 7.42        | 7.33        | 11.73         | 11.80         | 7.53        | 7.53        | 7.82        | 6.31      | 5.91      | 11.9<br>5  | 15.3<br>0  |
| Fe <sub>2</sub> O <sub>3</sub> | 22.16       | 22.30       | 22.09       | 22.25       | 2.05          | 1.69          | 21.82       | 22.99       | 21.81       | 15.81     | 15.96     | 1.29       | 10.2<br>6  |
| MnO                            | 0.30        | 0.29        | 0.28        | 0.30        | 0.03          | 0.01          | 0.26        | 0.26        | 0.28        | 0.23      | 0.23      | 0.01       | 0.16       |
| MgO                            | 9.92        | 9.91        | 9.20        | 9.97        | 0.10          | 0.09          | 9.12        | 9.91        | 9.29        | 15.99     | 17.13     | 0.07       | 7.29       |
| CaO                            | 13.97       | 13.50       | 13.76       | 12.68       | 0.52          | 0.38          | 13.89       | 13.30       | 13.28       | 13.07     | 12.83     | 0.22       | 10.5<br>2  |
| Na <sub>2</sub> O              | 1.46        | 1.68        | 1.38        | 1.68        | 2.11          | 2.57          | 1.43        | 0.98        | 1.87        | 2.08      | 2.17      | 2.26       | 3.16       |
| K <sub>2</sub> O               | 1.09        | 1.20        | 0.90        | 0.99        | 6.65          | 6.22          | 1.08        | 1.06        | 1.50        | 1.71      | 1.83      | 6.92       | 1.09       |
| P <sub>2</sub> O <sub>5</sub>  | 1.50        | 1.51        | 1.45        | 1.55        | 0.01          | 0.01          | 1.67        | 1.30        | 1.57        | 1.61      | 1.62      | 0.01       | 0.42       |
| SO <sub>3</sub>                | 0.13        | 0.14        | 0.21        | 0.10        | b.d.          | b.d.          | 0.03        | 0.07        | 0.03        | 0.17      | 0.16      | 0.00       | 0.01       |
| Cr <sub>2</sub> O <sub>3</sub> | 0.03        | 0.03        | 0.03        | 0.03        | b.d.          | b.d.          | 0.04        | 0.05        | 0.04        | 0.10      | 0.10      | 0.00       | 0.04       |
| NiO                            | 0.01        | 0.01        | 0.02        | 0.02        | b.d.          | b.d.          | 0.01        | 0.01        | 0.01        | 0.04      | 0.05      | 0.01       | 0.01       |
| H <sub>2</sub> O               | 0.65        | 0.51        | 0.57        | 0.77        | 0.08          | 0.20          | 0.38        | 0.40        | 0.17        | 0.35      | 0.26      | 0.08       | 0.14       |
| LOI                            | 1.88        | 1.54        | 2.23        | 2.38        | 0.52          | 0.75          | 1.58        | 1.73        | 1.06        | 1.19      | 0.63      | 0.34       | 0.56       |
| Sum                            | 99.54       | 99.02       | 99.20       | 99.04       | 98.79         | 99.25         | 99.18       | 99.19       | 99.26       | 99.28     | 98.54     | 99.2<br>5  | 99.3<br>0  |
| Zn                             | 158         | 160         | 158         | 163         | 43            | 66            | 151         | 160         | 154         | 128       | 130       | 14         | 97         |
| Cu                             | 63          | 58          | 58          | 64          | <5            | <5            | 34          | 35          | 38          | 54        | 58        | <5         | <5         |
| Ni                             | 70          | 71          | 60          | 73          | <5            | <5            | 33          | 40          | 35          | 328       | 415       | <5         | 61         |
| Co                             | 101         | 108         | 95          | 102         | <5            | <5            | 95          | 103         | 89          | 101       | 109       | <5         | 40         |
| Mn                             | 2578        | 2608        | 2493        | 2637        | 230           | 93            | 2254        | 2314        | 2333        | 2017      | 2021      | 67         | 1258       |
| Cr                             | 176         | 187         | 180         | 186         | 20            | 25            | 233         | 312         | 223         | 755       | 729       | 16         | 281        |
| V                              | 337         | 341         | 346         | 339         | 5             | 5             | 372         | 394         | 354         | 277       | 265       | 9          | 226        |
| Mo                             | -           | -           | -           | -           | -             | -             | <5          | <5          | <5          | <5        | <5        | <5         | <6         |
| Nb                             | 308         | 310         | 303         | 313         | 35            | 43            | 251         | 225         | 245         | 171       | 168       | <5         | 14         |
| Zr                             | 1021        | 1023        | 1035        | 1035        | 181           | 150           | 1021        | 982         | 1039        | 533       | 546       | 91         | 221        |
| Y                              | 29          | 28          | 30          | 31          | 109           | 121           | 32          | 27          | 29          | 31        | 32        | 9          | 43         |
| Sr                             | 2107        | 2059        | 2483        | 2387        | 52            | 33            | 1135        | 800         | 926         | 1404      | 1435      | 87         | 883        |
| Rb                             | 25          | 21          | 18          | 17          | 173           | 321           | 19          | 32          | 26          | 68        | 69        | 284        | 33         |
| U                              | 21          | 20          | 22          | 23          | <5            | <5            | 9           | 3           | 5           | 13        | 13        | <5         | <5         |
| Th                             | <5          | <5          | <5          | <5          | 29            | 45            | <5          | <5          | <5          | 7         | 8         | 13         | <5         |
| Pb                             | <5          | <5          | <5          | <5          | 29            | 26            | <5          | <5          | <5          | <5        | <5        | 38         | 13         |
| S                              | 1342        | 1302        | 3447        | 932         | <5            | 19            | 1470        | 2254        | 738         | 1671      | 1414      | 433        | 417        |
| Sc                             | 29          | 29          | 30          | 30          | <10           | <10           | 35          | 38          | 31          | 26        | 23        | <10        | 38         |
| Ba                             | 565         | 572         | 639         | 630         | 203           | 161           | 560         | 454         | 654         | 1149      | 1024      | 733        | 887        |

*The major oxide results are given in weight percentage and the trace element data are provided in parts per million by weight. The H<sub>2</sub>O content is calculated as the weight % lost upon heating to 110°C for 8 hours, while LOI is calculated as the weight % lost upon heating to 850 °C for 4 hours. "-" indicates that the samples was not analyzed for this element and >5 indicates that the amount detected was less than 5 ppm.*

Appendix D: Table 22 Continued:

| Sample:                        | DIK-10 | DIK-11 | DIK-12 | DIK-13 | DIK-CR1 | DIK-VM1 | DIK-VM2 | DIK-VM3 | DIK-VM4 | DSAT-1 | DSAT-2 | DSAT-3A | DSAT-3B | DSAT-4 | DSAT-CR1 |
|--------------------------------|--------|--------|--------|--------|---------|---------|---------|---------|---------|--------|--------|---------|---------|--------|----------|
| SiO <sub>2</sub>               | 30.55  | 31.35  | 30.24  | 30.93  | 74.80   | 33.02   | 33.11   | 32.99   | 33.11   | 34.51  | 34.01  | 34.16   | 33.87   | 33.97  | 75.38    |
| TiO <sub>2</sub>               | 6.48   | 6.90   | 6.41   | 6.70   | 0.18    | 5.75    | 5.78    | 5.96    | 5.78    | 6.78   | 6.93   | 6.87    | 6.90    | 6.58   | 0.26     |
| Al <sub>2</sub> O <sub>3</sub> | 5.81   | 6.12   | 5.75   | 5.97   | 12.03   | 7.83    | 7.87    | 6.91    | 6.67    | 8.95   | 8.52   | 8.41    | 8.52    | 8.19   | 11.98    |
| Fe <sub>2</sub> O <sub>3</sub> | 19.06  | 19.17  | 18.77  | 19.11  | 2.20    | 17.36   | 17.57   | 17.60   | 17.54   | 18.74  | 19.90  | 19.75   | 19.82   | 20.02  | 1.49     |
| MnO                            | 0.26   | 0.25   | 0.27   | 0.26   | 0.02    | 0.24    | 0.24    | 0.24    | 0.24    | 0.24   | 0.25   | 0.26    | 0.25    | 0.27   | 0.02     |
| MgO                            | 12.43  | 11.49  | 12.25  | 11.95  | 0.13    | 12.08   | 12.38   | 13.13   | 10.82   | 6.72   | 8.05   | 8.29    | 8.02    | 9.29   | 0.19     |
| CaO                            | 16.27  | 16.10  | 16.10  | 15.79  | 0.84    | 12.87   | 12.62   | 12.94   | 16.25   | 15.17  | 13.75  | 13.96   | 13.65   | 14.68  | 0.79     |
| Na <sub>2</sub> O              | 1.53   | 1.29   | 1.97   | 1.36   | 2.27    | 0.68    | 1.35    | 0.83    | 0.58    | 2.14   | 2.02   | 2.07    | 2.00    | 1.82   | 2.72     |
| K <sub>2</sub> O               | 3.44   | 2.30   | 3.02   | 3.64   | 5.93    | 1.49    | 1.00    | 1.13    | 1.96    | 1.20   | 1.16   | 1.32    | 1.21    | 1.10   | 4.82     |
| P <sub>2</sub> O <sub>5</sub>  | 2.30   | 2.07   | 2.27   | 2.15   | 0.05    | 2.17    | 2.20    | 2.28    | 2.17    | 1.56   | 1.47   | 1.49    | 1.42    | 1.62   | 0.06     |
| SO <sub>3</sub>                | 0.80   | 0.08   | 1.52   | 0.80   | b.d.    | 0.01    | 0.01    | 0.01    | 0.08    | 0.10   | 0.07   | 0.08    | 0.08    | 0.04   | -0.01    |
| Cr <sub>2</sub> O <sub>3</sub> | 0.07   | 0.07   | 0.06   | 0.06   | b.d.    | 0.07    | 0.07    | 0.07    | 0.07    | 0.01   | 0.03   | 0.03    | 0.02    | 0.05   | 0.00     |
| NiO                            | 0.04   | 0.03   | 0.04   | 0.03   | b.d.    | 0.03    | 0.03    | 0.03    | 0.03    | 0.01   | 0.01   | 0.01    | 0.01    | 0.01   | 0.01     |
| H <sub>2</sub> O               | 0.23   | 0.45   | 0.29   | 0.21   | 0.13    | 1.62    | 1.32    | 1.49    | 0.73    | 0.50   | 0.40   | 0.39    | 0.34    | 0.50   | 0.21     |
| LOI                            | 0.75   | 2.10   | 0.34   | 0.50   | 0.83    | 3.96    | 3.58    | 3.56    | 3.33    | 2.41   | 2.25   | 1.90    | 2.14    | 1.99   | 0.71     |
| Sum                            | ####   | 99.77  | 99.30  | 99.48  | 99.40   | 99.17   | 99.12   | 99.16   | 99.36   | 99.05  | 98.81  | 98.98   | 98.26   | 100.14 | 98.63    |
| Zn                             | 149    | 150    | 146    | 148    | 25      | 134     | 135     | 139     | 142     | 146    | 148    | 149     | 147     | 152    | 34       |
| Cu                             | 72     | 70     | 77     | 76     | <5      | 69      | 64      | 76      | 65      | 69     | 66     | 66      | 68      | 65     | <5       |
| Ni                             | 280    | 202    | 280    | 262    | <5      | 163     | 175     | 162     | 165     | 26     | 46     | 50      | 43      | 66     | <5       |
| Co                             | 102    | 95     | 99     | 98     | <5      | 70      | 71      | 74      | 70      | 67     | 76     | 80      | 81      | 85     | <5       |
| Mn                             | 2263   | 2191   | 2242   | 2184   | 162     | 1902    | 1951    | 1995    | 1994    | 2123   | 2165   | 2209    | 2134    | 2349   | 180      |
| Cr                             | 439    | 489    | 435    | 417    | 12      | 415     | 459     | 440     | 431     | <5     | 144    | 150     | 126     | 320    | 16       |
| V                              | 346    | 359    | 335    | 364    | 9       | 388     | 413     | 414     | 408     | 332    | 341    | 342     | 337     | 337    | 16       |
| Mo                             | -      | -      | -      | -      | -       | <10     | <10     | <10     | <10     | <5     | <5     | <5      | <5      | <5     | <5       |
| Nb                             | 211    | 225    | 209    | 207    | 7       | 182     | 188     | 191     | 192     | 268    | 255    | 258     | 244     | 273    | 12       |
| Zr                             | 773    | 779    | 785    | 810    | 210     | 805     | 828     | 821     | 883     | 1274   | 1204   | 1188    | 1206    | 1124   | 166      |
| Y                              | 35     | 30     | 32     | 33     | 15      | 34      | 36      | 37      | 36      | 32     | 32     | 36      | 32      | 32     | 27       |
| Sr                             | 1811   | 1530   | 1675   | 1700   | 124     | 1455    | 1515    | 1543    | 1707    | 1651   | 1545   | 1601    | 1474    | 1839   | 151      |
| Rb                             | 132    | 96     | 112    | 140    | 223     | 79      | 75      | 75      | 101     | 41     | 37     | 46      | 45      | 50     | 213      |
| U                              | 18     | 15     | 17     | 15     | <5      | 14      | 13      | 16      | 13      | 11     | 11     | 13      | 8       | 14     | <5       |
| Th                             | <5     | <5     | <5     | <5     | 12      | <5      | <5      | <5      | <5      | <5     | <5     | <5      | <5      | <5     | 23       |
| Pb                             | <5     | <5     | <5     | <5     | 35      | <5      | <5      | 5       | <5      | <5     | <5     | <5      | <5      | <5     | 28       |
| S                              | 4289   | 543    | 8196   | 4173   | <5      | 360     | 281     | 280     | 455     | 2056   | 1743   | 1859    | 1797    | 2199   | 185      |
| Sc                             | 26     | 30     | 28     | 29     | <10     | 29      | 28      | 30      | 30      | 28     | 30     | 27      | 28      | 27     | <10      |
| Ba                             | 1113   | 926    | 747    | 1270   | 753     | 1435    | 1287    | 1404    | 1193    | 743    | 739    | 820     | 890     | 713    | 786      |

*The major oxide results are given in weight percentage and the trace element data are provided in parts per million by weight. The H<sub>2</sub>O content is calculated as the weight % lost upon heating to 110°C for 8 hours, while LOI is calculated as the weight % lost upon heating to 850 °C for 4 hours. "-" indicates that the samples was not analyzed for this element and >5 indicates that the amount detected was less than 5 ppm.*

**Appendix D: Table 22 Continued:**

| Sample:                        | LOU-2 | LOU-2<br>Rep 1 | LOU-3 | LOU-4 | LOU-<br>CR-1 | RTPT-1 | ZAND-7 |
|--------------------------------|-------|----------------|-------|-------|--------------|--------|--------|
| SiO <sub>2</sub>               | 31.85 | 31.69          | 31.33 | 31.92 | 71.61        | 75.63  | 30.61  |
| TiO <sub>2</sub>               | 6.77  | 6.71           | 6.25  | 6.71  | 0.34         | 0.18   | 6.89   |
| Al <sub>2</sub> O <sub>3</sub> | 6.93  | 6.92           | 6.75  | 6.87  | 12.92        | 11.03  | 6.04   |
| Fe <sub>2</sub> O <sub>3</sub> | 19.37 | 19.39          | 18.39 | 19.37 | 2.91         | 2.49   | 18.12  |
| MnO                            | 0.29  | 0.30           | 0.30  | 0.29  | 0.04         | 0.04   | 0.27   |
| MgO                            | 11.48 | 11.42          | 11.45 | 11.55 | 0.39         | 0.01   | 10.30  |
| CaO                            | 15.76 | 15.49          | 16.86 | 15.43 | 1.39         | 0.70   | 14.55  |
| Na <sub>2</sub> O              | 1.41  | 1.41           | 2.20  | 1.88  | 2.96         | 2.50   | 2.05   |
| K <sub>2</sub> O               | 2.19  | 2.30           | 3.00  | 3.06  | 4.68         | 5.50   | 2.59   |
| P <sub>2</sub> O <sub>5</sub>  | 1.66  | 1.63           | 1.91  | 1.65  | 0.17         | 0.02   | 1.74   |
| SO <sub>3</sub>                | 0.14  | 0.16           | 0.41  | 0.27  | 0.00         | b.d.   | 0.13   |
| Cr <sub>2</sub> O <sub>3</sub> | 0.06  | 0.06           | 0.06  | 0.06  | 0.00         | b.d.   | 0.05   |
| NiO                            | 0.03  | 0.03           | 0.03  | 0.03  | 0.01         | 0.01   | 0.02   |
| H <sub>2</sub> O               | 0.28  | 0.26           | 0.09  | 0.09  | 0.15         | 0.44   | 0.43   |
| LOI                            | 1.01  | 0.99           | -0.43 | -0.08 | 0.91         | 0.73   | 3.42   |
| Sum                            | 99.24 | 98.76          | 98.60 | 99.10 | 98.49        | 99.28  | 97.13  |
| Zn                             | 146   | 145            | 147   | 145   | 34           | 58     | -      |
| Cu                             | 85    | 83             | 79    | 82    | <5           | <5     | 159    |
| Ni                             | 209   | 211            | 209   | 211   | <5           | <5     | -      |
| Co                             | 99    | 101            | 91    | 98    | <5           | <5     | -      |
| Mn                             | 2559  | 2581           | 2607  | 2579  | 338          | 293    | 371    |
| Cr                             | 380   | 399            | 432   | 391   | 17           | 20     | 400    |
| V                              | 363   | 365            | 364   | 367   | 25           | 9      | -      |
| Mo                             | <5    | <5             | <5    | <5    | <5           | <5     | 271    |
| Nb                             | 273   | 274            | 287   | 270   | 10           | 41     | 1056   |
| Zr                             | 777   | 792            | 787   | 770   | 177          | 267    | 31     |
| Y                              | 27    | 31             | 37    | 29    | 32           | 94     | 2187   |
| Sr                             | 2358  | 2321           | 2473  | 2191  | 91           | 35     | 134    |
| Rb                             | 74    | 74             | 85    | 87    | 212          | 267    | 18     |
| U                              | 26    | 26             | 29    | 24    | <5           | <5     | <5     |
| Th                             | <5    | <5             | <5    | <5    | 14           | 20     | <5     |
| Pb                             | <5    | <5             | <5    | <5    | 18           | 33     | -      |
| S                              | 1330  | 1312           | 2892  | 1786  | 43           | <5     | 21     |
| Sc                             | 25    | 27             | 27    | 26    | <10          | <10    | 7374   |
| Ba                             | 889   | 871            | 851   | 826   | 546          | 361    | -      |

*The major oxide results are given in weight percentage and the trace element data are provided in parts per million by weight. The H<sub>2</sub>O content is calculated as the weight % lost upon heating to 110°C for 8 hours, while LOI is calculated as the weight % lost upon heating to 850 °C for 4 hours. "-" indicates that the samples were not analyzed for this element and >5 indicates that the amount detected was less than 5 ppm.*

## 10.5. Appendix E: Trace element concentrations by ICP-MS.

**Appendix E: Table 23: ICP-MS trace element concentrations of Namaqualand melilitites & country rocks.**

| Locality | -----Louisfontein----- |       |       | -----Biesiesfontein A----- |         |         |         | -----Biesiesfontein B----- |         |         |
|----------|------------------------|-------|-------|----------------------------|---------|---------|---------|----------------------------|---------|---------|
| Element  | LOU-2                  | LOU-3 | LOU-4 | BIES-10                    | BIES-11 | BIESA-1 | BIESA-2 | BIESB-1                    | BIESB-2 | BIESB-3 |
| Sc       | 19.6                   | 20.2  | 18.6  | 17.7                       | 17.3    | 18.9    | 17.3    | 16.2                       | 16.5    | 14.9    |
| V        | 376                    | 425   | 356   | 385                        | 357     | 377     | 364     | 337                        | 329     | 301     |
| Cr       | 418                    | 454   | 413   | 488                        | 452     | 487     | 464     | 583                        | 602     | 520     |
| Co       | 77.8                   | 90.1  | 74.0  | 94.8                       | 89.4    | 93.9    | 91.1    | 86.4                       | 81.6    | 77.3    |
| Ni       | 228                    | 196   | 220   | 305                        | 298     | 319     | 301     | 383                        | 348     | 336     |
| Cu       | 107.2                  | 97.1  | 106.6 | 97.2                       | 94.0    | 95.6    | 92.7    | 81.4                       | 76.6    | 75.6    |
| Zn       | 198                    | 153   | 407   | 201                        | 244     | 181     | 210     | 185                        | 187     | 276     |
| Rb       | 77.4                   | 65.5  | 89.5  | 123.0                      | 140.1   | 163.8   | 135.5   | 112.6                      | 102.8   | 78.9    |
| Sr       | 2339                   | 2164  | 2116  | 1263                       | 1203    | 1176    | 1197    | 1595                       | 1327    | 1521    |
| Y        | 30.9                   | 32.9  | 30.4  | 24.5                       | 23.8    | 24.1    | 24.3    | 28.6                       | 26.8    | 27.7    |
| Zr       | 844                    | 836   | 828   | 789                        | 804     | 711     | 800     | 762                        | 726     | 716     |
| Nb       | 273                    | 310   | 262   | 221                        | 206     | 211     | 213     | 184                        | 175     | 173     |
| Cs       | 0.554                  | 0.280 | 0.759 | 1.04                       | 1.17    | 1.43    | 1.22    | 0.851                      | 0.389   | 0.342   |
| Ba       | 814                    | 821   | 768   | 1399                       | 1237    | 1028    | 1274    | 639                        | 834     | 784     |
| La       | 172                    | 181   | 171   | 81                         | 79      | 85      | 82      | 86                         | 81      | 84      |
| Ce       | 325                    | 321   | 327   | 176                        | 172     | 184     | 180     | 195                        | 190     | 193     |
| Pr       | 37.0                   | 36.0  | 37.3  | 22.7                       | 22.1    | 23.9    | 23.3    | 25.4                       | 24.0    | 25.2    |
| Nd       | 134                    | 133   | 136   | 90.6                       | 89.8    | 96.2    | 93.7    | 102.4                      | 98.3    | 103     |
| Sm       | 21.5                   | 20.7  | 21.8  | 16.5                       | 16.1    | 17.4    | 16.9    | 19.2                       | 18.2    | 19.0    |
| Eu       | 6.07                   | 5.72  | 5.89  | 4.62                       | 4.50    | 4.74    | 4.58    | 5.44                       | 5.05    | 5.27    |
| Gd       | 15.4                   | 15.1  | 15.0  | 11.8                       | 11.5    | 12.1    | 11.9    | 13.8                       | 13.1    | 13.3    |
| Tb       | 1.90                   | 1.76  | 1.85  | 1.42                       | 1.45    | 1.51    | 1.49    | 1.68                       | 1.61    | 1.63    |
| Dy       | 8.14                   | 8.09  | 8.16  | 6.20                       | 6.14    | 6.37    | 6.45    | 7.51                       | 7.05    | 7.31    |
| Ho       | 1.29                   | 1.24  | 1.25  | 0.99                       | 0.95    | 1.00    | 0.99    | 1.20                       | 1.15    | 1.14    |
| Er       | 2.81                   | 2.62  | 2.75  | 2.16                       | 2.08    | 2.20    | 2.20    | 2.60                       | 2.45    | 2.55    |
| Tm       | 0.337                  | 0.288 | 0.345 | 0.255                      | 0.262   | 0.254   | 0.267   | 0.318                      | 0.297   | 0.311   |
| Yb       | 1.71                   | 1.67  | 1.67  | 1.45                       | 1.44    | 1.39    | 1.45    | 1.62                       | 1.58    | 1.56    |
| Lu       | 0.211                  | 0.197 | 0.218 | 0.179                      | 0.174   | 0.175   | 0.190   | 0.211                      | 0.195   | 0.192   |
| Hf       | 18.8                   | 16.1  | 18.1  | 19.3                       | 17.7    | 16.8    | 18.0    | 15.6                       | 14.8    | 14.8    |
| Ta       | 19.9                   | 20.8  | 18.0  | 17.9                       | 12.0    | 13.5    | 13.9    | 15.3                       | 14.7    | 14.7    |
| Pb       | 2.38                   | 1.50  | 5.58  | 2.47                       | 2.68    | 2.12    | 2.29    | 2.65                       | 2.57    | 3.35    |
| Th       | 7.67                   | 7.23  | 7.49  | 11.91                      | 10.89   | 11.70   | 11.46   | 9.54                       | 9.00    | 9.42    |
| U        | 12.7                   | 13.2  | 12.0  | 8.34                       | 6.94    | 7.36    | 7.62    | 12.4                       | 11.9    | 12.1    |

***All concentrations are reported in parts per million. See section 3.7.3 for a details of the sample preparation and analytical techniques used and estimated precisions. See Table 3 for the concentrations of rock standards analyzed as unknowns during the course of this study their reproducibility and comparison with accepted values.***

**Appendix E: Table 23: Continued.**

| Locality | -----Biesiesfontein C----- |         |         | -----Biesiesfontein D----- |         |         |         | -----Biesiesfontein E----- |         |         |
|----------|----------------------------|---------|---------|----------------------------|---------|---------|---------|----------------------------|---------|---------|
| Element  | BIESC-1                    | BIESC-2 | BIESC-3 | BIESD-1                    | BIESD-2 | BIESD-3 | BIESD-4 | BIESE-1                    | BIESE-2 | BIESE-3 |
| Sc       | 18.3                       | 19.3    | 19.2    | 20.1                       | 19.4    | 21.0    | 20.5    | 28.4                       | 29.2    | 26.0    |
| V        | 270                        | 301     | 285     | 312                        | 311     | 302     | 312     | 371                        | 377     | 349     |
| Cr       | 405                        | 438     | 442     | 223                        | 227     | 210     | 232     | 272                        | 340     | 263     |
| Co       | 72.5                       | 71.8    | 80.8    | 101.0                      | 107.6   | 94.6    | 102.0   | 67.0                       | 74.3    | 64.4    |
| Ni       | 211                        | 184     | 238     | 36                         | 40      | 23      | 41      | 5                          | 14      | 5       |
| Cu       | 70.5                       | 78.5    | 74.0    | 87.8                       | 86.9    | 83.4    | 89.5    | 63.0                       | 64.1    | 62.6    |
| Zn       | 245                        | 311     | 185     | 158                        | 160     | 158     | 163     | 196                        | 225     | 217     |
| Rb       | 53.4                       | 54.2    | 41.5    | 27.9                       | 23.6    | 22.1    | 21.1    | 19.8                       | 33.1    | 26.5    |
| Sr       | 1819                       | 2058    | 2082    | 1869                       | 1804    | 2157    | 2144    | 1167                       | 813     | 922     |
| Y        | 33.7                       | 36.0    | 35.5    | 29.4                       | 29.5    | 28.9    | 30.0    | 27.6                       | 24.2    | 26.2    |
| Zr       | 810                        | 951     | 851     | 1094                       | 1076    | 1048    | 1088    | 1156                       | 1095    | 1158    |
| Nb       | 227                        | 265     | 255     | 295                        | 295     | 276     | 294     | 258                        | 231     | 248     |
| Cs       | 0.687                      | 0.431   | 0.533   | 0.317                      | 0.440   | 0.324   | 0.495   | 0.428                      | 0.221   | 0.559   |
| Ba       | 603                        | 763     | 649     | 484                        | 484     | 534     | 546     | 504                        | 410     | 576     |
| La       | 228                        | 247     | 239     | 125                        | 124     | 114     | 127     | 141                        | 115     | 120     |
| Ce       | 393                        | 421     | 401     | 243                        | 238     | 226     | 248     | 277                        | 225     | 237     |
| Pr       | 40.5                       | 45.0    | 42.9    | 27.8                       | 27.7    | 26.2    | 28.5    | 31.9                       | 26.5    | 27.6    |
| Nd       | 141                        | 155     | 147     | 104                        | 103     | 98.5    | 106     | 121                        | 99.6    | 105     |
| Sm       | 21.5                       | 23.8    | 22.4    | 17.5                       | 17.4    | 17.0    | 18.0    | 19.9                       | 16.6    | 17.9    |
| Eu       | 5.85                       | 6.47    | 6.29    | 4.82                       | 4.75    | 4.70    | 4.84    | 5.56                       | 4.68    | 5.15    |
| Gd       | 15.2                       | 16.2    | 15.7    | 13.1                       | 13.0    | 12.5    | 13.3    | 14.5                       | 11.9    | 13.2    |
| Tb       | 1.92                       | 2.07    | 2.03    | 1.57                       | 1.55    | 1.51    | 1.60    | 1.72                       | 1.50    | 1.61    |
| Dy       | 8.57                       | 9.27    | 9.02    | 7.26                       | 7.17    | 6.95    | 7.21    | 7.84                       | 6.62    | 7.34    |
| Ho       | 1.41                       | 1.47    | 1.46    | 1.15                       | 1.14    | 1.14    | 1.16    | 1.23                       | 1.05    | 1.15    |
| Er       | 3.19                       | 3.25    | 3.29    | 2.46                       | 2.44    | 2.38    | 2.48    | 2.40                       | 2.37    | 2.46    |
| Tm       | 0.389                      | 0.419   | 0.421   | 0.289                      | 0.280   | 0.280   | 0.288   | 0.306                      | 0.286   | 0.299   |
| Yb       | 2.06                       | 2.11    | 2.13    | 1.69                       | 1.67    | 1.67    | 1.68    | 1.58                       | 1.46    | 1.56    |
| Lu       | 0.255                      | 0.274   | 0.276   | 0.201                      | 0.208   | 0.199   | 0.209   | 0.189                      | 0.180   | 0.197   |
| Hf       | 16.5                       | 19.3    | 16.9    | 23.8                       | 23.5    | 23.0    | 23.8    | 26.1                       | 25.5    | 26.0    |
| Ta       | 14.1                       | 16.0    | 16.8    | 25.2                       | 25.2    | 24.3    | 25.1    | 25.3                       | 21.9    | 23.4    |
| Pb       | 3.32                       | 4.02    | 1.49    | 1.29                       | 1.76    | 1.56    | 1.77    | 0.96                       | 1.44    | 1.35    |
| Th       | 10.41                      | 10.97   | 10.71   | 4.20                       | 4.24    | 3.58    | 4.37    | 5.05                       | 4.17    | 4.44    |
| U        | 8.08                       | 8.96    | 8.49    | 8.96                       | 9.19    | 8.02    | 9.28    | 4.33                       | 3.70    | 4.12    |

**Appendix E: Table 23: Continued.**

| Locality | -----Zandkopsdrift----- |         |         | ----Waterval---- |       | -----Dikdoorn Satellite----- |        |         |         |        |
|----------|-------------------------|---------|---------|------------------|-------|------------------------------|--------|---------|---------|--------|
| Element  | ZAND-1*                 | ZAND-4* | ZAND-7* | WAT-1            | WAT-2 | DSAT-1                       | DSAT-2 | DSAT-3A | DSAT-3B | DSAT-4 |
| Sc       | 24.0                    | 23.4    | 13.7    | 18.9             | 16.2  | 18.4                         | 23.1   | 22.0    | 19.9    | 20.6   |
| V        | n.a.                    | n.a.    | n.a.    | 285              | 263   | 303                          | 360    | 347     | 328     | 339    |
| Cr       | n.a.                    | n.a.    | n.a.    | 746              | 684   | 33                           | 195    | 193     | 164     | 364    |
| Co       | n.a.                    | n.a.    | n.a.    | 82.2             | 87.4  | 45.6                         | 60.9   | 59.7    | 55.3    | 63.0   |
| Ni       | n.a.                    | n.a.    | n.a.    | 394              | 492   | 5.2                          | 19.1   | 22.4    | 16.2    | 47.5   |
| Cu       | n.a.                    | n.a.    | n.a.    | 69.0             | 71.8  | 93.4                         | 95.0   | 91.0    | 88.0    | 88.7   |
| Zn       | n.a.                    | n.a.    | n.a.    | 169              | 237   | 187                          | 261    | 250     | 238     | 177    |
| Rb       | 135                     | 124     | 126     | 72.0             | 70.1  | 44.0                         | 43.1   | 49.3    | 46.1    | 53.5   |
| Sr       | 2463                    | 1681    | 2028    | 1425             | 1309  | 1544                         | 1640   | 1621    | 1385    | 1783   |
| Y        | 40.0                    | 43.7    | 33.3    | 31.4             | 30.3  | 28.3                         | 30.7   | 29.0    | 27.0    | 30.3   |
| Zr       | 851                     | 825     | 1017    | 560              | 561   | 1357                         | 1410   | 1300    | 1262    | 1217   |
| Nb       | 252                     | 259     | 251     | 168              | 164   | 258                          | 272    | 263     | 232     | 279    |
| Cs       | 0.756                   | 1.093   | 1.397   | 0.795            | 0.524 | 0.841                        | 0.814  | 0.656   | 0.688   | 0.473  |
| Ba       | 5563                    | 3500    | 6731    | 893              | 700   | 651                          | 717    | 730     | 783     | 618    |
| La       | 127                     | 157     | 119     | 110              | 108   | 79                           | 98     | 94      | 72      | 131    |
| Ce       | 256                     | 311     | 239     | 233              | 229   | 171                          | 207    | 195     | 159     | 247    |
| Pr       | 29.6                    | 35.1    | 30.1    | 27.8             | 27.5  | 22.2                         | 26.0   | 24.4    | 20.6    | 28.9   |
| Nd       | 120                     | 139     | 117     | 108              | 108   | 90.5                         | 104    | 95.3    | 84.1    | 108    |
| Sm       | 22.4                    | 25.1    | 19.0    | 18.6             | 18.9  | 17.3                         | 19.1   | 17.5    | 16.3    | 18.9   |
| Eu       | 6.27                    | 7.01    | 5.16    | 5.29             | 5.34  | 5.02                         | 5.49   | 5.20    | 4.69    | 5.47   |
| Gd       | 16.1                    | 17.6    | 13.5    | 14.0             | 13.9  | 13.1                         | 14.4   | 13.4    | 12.1    | 13.7   |
| Tb       | 1.95                    | 2.14    | 1.67    | 1.77             | 1.72  | 1.67                         | 1.81   | 1.66    | 1.58    | 1.72   |
| Dy       | 8.86                    | 9.74    | 7.38    | 7.86             | 7.52  | 7.66                         | 8.16   | 7.59    | 7.12    | 7.71   |
| Ho       | 1.37                    | 1.50    | 1.19    | 1.30             | 1.27  | 1.24                         | 1.33   | 1.23    | 1.16    | 1.23   |
| Er       | 2.87                    | 3.11    | 2.76    | 2.87             | 2.83  | 2.65                         | 2.90   | 2.68    | 2.56    | 2.75   |
| Tm       | 0.324                   | 0.352   | 0.304   | 0.371            | 0.352 | 0.324                        | 0.367  | 0.337   | 0.309   | 0.349  |
| Yb       | 1.65                    | 1.81    | 1.64    | 1.91             | 1.78  | 1.74                         | 1.88   | 1.75    | 1.58    | 1.82   |
| Lu       | 0.226                   | 0.249   | 0.215   | 0.247            | 0.219 | 0.222                        | 0.244  | 0.228   | 0.198   | 0.217  |
| Hf       | 18.9                    | 18.6    | 22.0    | 11.3             | 11.2  | 27.7                         | 29.3   | 27.3    | 27.2    | 25.5   |
| Ta       | 21.7                    | 22.5    | 16.0    | 8.3              | 8.9   | 24.2                         | 24.9   | 23.4    | 22.4    | 22.7   |
| Pb       | 183                     | 4.55    | 6.89    | 4.07             | 4.05  | 2.00                         | 3.23   | 3.28    | 2.49    | 2.31   |
| Th       | 8.75                    | 10.5    | 7.76    | 13.9             | 13.9  | 4.28                         | 4.98   | 4.69    | 3.90    | 5.78   |
| U        | 8.76                    | 8.98    | 8.19    | 7.30             | 7.03  | 4.71                         | 5.28   | 4.92    | 4.21    | 6.78   |

*\*Zandkopsdrift melilitite data are from Ogungbuyi et al. (2022). "n.a." indicates not analyzed.*

**Appendix E: Table 23: Continued.**

| Locality | -----Dikdoorn----- |        |        |        | -----Koegel Fontein country rocks----- |           |           | Namaqualand gneiss country rocks |          |         |
|----------|--------------------|--------|--------|--------|----------------------------------------|-----------|-----------|----------------------------------|----------|---------|
| Element  | DIK-10             | DIK-11 | DIK-12 | DIK-13 | RTPT-1                                 | BIESD-CR1 | BIESD-CR2 | LOU-CR1                          | DSAT-CR1 | DIK-CR1 |
| Sc       | 20.5               | 23.0   | 20.0   | 20.3   | <0.1                                   | 0.5       | 0.7       | 2.60                             | 0.094    | <0.1    |
| V        | 310                | 333    | 300    | 332    | 5                                      | 3         | 4         | 17.7                             | 15.0     | 11      |
| Cr       | 478                | 545    | 467    | 457    | 19                                     | 20        | 20        | 14.4                             | 18.8     | 15      |
| Co       | 102                | 95.2   | 99.0   | 98.0   | n.d.                                   | n.d.      | n.d.      | 2.23                             | 1.12     | n.d.    |
| Ni       | 276                | 178    | 264    | 248    | 31                                     | 34        | 34        | 4.46                             | 10.9     | 24      |
| Cu       | 97.6               | 95.2   | 101    | 98.6   | 13.8                                   | 13.1      | 13.6      | 8.55                             | 8.90     | 11.6    |
| Zn       | 149                | 150    | 146    | 148    | n.a.                                   | n.a.      | n.a.      | 30.0                             | 30.7     | n.a.    |
| Rb       | 132.4              | 97.2   | 110    | 140    | 229                                    | 142       | 268       | 93.2                             | 134      | 193     |
| Sr       | 1667               | 1425   | 1545   | 1581   | 21                                     | 21        | 10        | 31.0                             | 26.7     | 92      |
| Y        | 31.5               | 32.4   | 31.8   | 30.9   | 39.4                                   | 64.0      | 18.5      | 18.0                             | 6.56     | 16.1    |
| Zr       | 799                | 835    | 819    | 841    | 283                                    | 166       | 142       | 124                              | 156      | 245     |
| Nb       | 194                | 217    | 193    | 189    | 34                                     | 32        | 37        | 5.13                             | 8.95     | 6.11    |
| Cs       | 0.957              | 0.737  | 0.907  | 0.966  | 1.741                                  | 0.785     | 1.053     | 0.668                            | 0.875    | 0.932   |
| Ba       | 1017               | 816    | 663    | 1152   | 317                                    | 117       | 85        | 298                              | 109      | 718     |
| La       | 101                | 98     | 101    | 95     | 33                                     | 62        | 10        | 16.9                             | 7.84     | 40      |
| Ce       | 229                | 224    | 228    | 216    | 93                                     | 117       | 49        | 29.6                             | 11.5     | 91      |
| Pr       | 29.7               | 29.2   | 29.9   | 28.2   | 8.6                                    | 15.9      | 3.1       | 4.50                             | 2.15     | 9.6     |
| Nd       | 121                | 119    | 122    | 116    | 31.3                                   | 59.1      | 11.2      | 17.3                             | 8.14     | 34.7    |
| Sm       | 22.3               | 22.3   | 22.5   | 21.5   | 6.7                                    | 11.9      | 2.5       | 4.11                             | 1.93     | 6.2     |
| Eu       | 6.09               | 6.09   | 6.15   | 5.76   | 0.36                                   | 0.85      | 0.10      | 0.642                            | 0.291    | 1.03    |
| Gd       | 16.2               | 16.2   | 16.3   | 15.4   | 6.4                                    | 11.1      | 2.4       | 4.38                             | 1.83     | 4.7     |
| Tb       | 1.96               | 2.00   | 1.93   | 1.88   | 1.16                                   | 1.84      | 0.48      | 0.690                            | 0.276    | 0.62    |
| Dy       | 8.52               | 8.77   | 8.56   | 8.28   | 7.27                                   | 10.91     | 3.21      | 4.23                             | 1.79     | 3.10    |
| Ho       | 1.34               | 1.41   | 1.34   | 1.34   | 1.60                                   | 2.44      | 0.75      | 0.818                            | 0.354    | 0.57    |
| Er       | 2.81               | 2.89   | 2.77   | 2.74   | 4.89                                   | 7.11      | 2.52      | 2.33                             | 1.06     | 1.43    |
| Tm       | 0.327              | 0.340  | 0.328  | 0.320  | 0.772                                  | 1.095     | 0.456     | 0.321                            | 0.152    | 0.205   |
| Yb       | 1.84               | 1.86   | 1.85   | 1.84   | 4.79                                   | 6.47      | 3.21      | 1.98                             | 1.10     | 1.25    |
| Lu       | 0.226              | 0.226  | 0.236  | 0.229  | 0.691                                  | 0.977     | 0.478     | 0.298                            | 0.176    | 0.187   |
| Hf       | 16.8               | 17.6   | 17.1   | 17.9   | 8.4                                    | 6.1       | 5.9       | 4.48                             | 5.82     | 6.9     |
| Ta       | 17.5               | 19.3   | 17.5   | 17.5   | 1.7                                    | 2.0       | 2.1       | 0.426                            | 0.578    | 0.3     |
| Pb       | 2.50               | 3.24   | 7.95   | 2.41   | 32.0                                   | 27.4      | 22.3      | 14.9                             | 24.0     | 40.7    |
| Th       | 11.0               | 12.3   | 11.2   | 10.6   | 11.0                                   | 15.6      | 4.38      | 11.1                             | 9.78     | 11.7    |
| U        | 9.06               | 8.90   | 9.34   | 8.84   | 2.30                                   | 4.43      | 4.39      | 0.993                            | 1.90     | 1.18    |

**"n.a" indicates not analyzed.**

## 10.6. Appendix F : Radiogenic isotope ratios.

**Appendix F: Table 24: Sr, Nd and Hf isotope compositions of Namaqualand melilitites.**

| Sample   | $^{87}\text{Sr}/^{86}\text{Sr}_m$ | $^{87}\text{Rb}/^{86}\text{Sr}$ | $^{87}\text{Sr}/^{86}\text{Sr}_i$ | $^{143}\text{Nd}/^{144}\text{Nd}_m$ | $^{143}\text{Nd}/^{144}\text{Nd}_i$ | $\epsilon_{\text{Nd}}(t)$ | $^{176}\text{Hf}/^{177}\text{Hf}_m$ | $^{176}\text{Hf}/^{177}\text{Hf}_i$ | $\epsilon_{\text{Hf}}(t)$ |
|----------|-----------------------------------|---------------------------------|-----------------------------------|-------------------------------------|-------------------------------------|---------------------------|-------------------------------------|-------------------------------------|---------------------------|
| LOU-3    | 0.70331                           | 0.0876                          | 0.70324                           | 0.512777                            | 0.512743                            | +3.6                      |                                     |                                     |                           |
| LOU-3L   | 0.70319                           | 0.0056                          | 0.70319                           |                                     |                                     |                           |                                     |                                     |                           |
| LOU-4    | 0.70335                           | 0.1223                          | 0.70325                           | 0.512782                            | 0.512748                            | +3.7                      | 0.282733                            | 0.282731                            | -0.6                      |
| LOU-4L   | 0.70321                           | 0.0199                          | 0.70319                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESA-1  | 0.70368                           | 0.4027                          | 0.70336                           | 0.512777                            | 0.512738                            | +3.5                      | 0.282735                            | 0.282733                            | -0.5                      |
| BIESA-1L | 0.70323                           | 0.0125                          | 0.70322                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESA-2  | 0.70377                           | 0.3274                          | 0.70351                           | 0.512784                            | 0.512744                            | +3.6                      |                                     |                                     |                           |
| BIESA-2L | 0.70325                           | 0.0183                          | 0.70323                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESB-1  | 0.70348                           | 0.2043                          | 0.70332                           | 0.512777                            | 0.512736                            | +3.4                      |                                     |                                     |                           |
| BIESB-1L | 0.70322                           | 0.0229                          | 0.70320                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESB-3  | 0.70340                           | 0.1501                          | 0.70328                           | 0.512769                            | 0.512729                            | +3.3                      |                                     |                                     |                           |
| BIESB-3L | 0.70321                           | 0.0431                          | 0.70318                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESC-2  | 0.70333                           | 0.0761                          | 0.70326                           | 0.512772                            | 0.512739                            | +3.5                      |                                     |                                     |                           |
| BIESC-2L | 0.70322                           | 0.0152                          | 0.70320                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESC-3  | 0.70328                           | 0.0577                          | 0.70324                           | 0.512759                            | 0.512726                            | +3.3                      | 0.282740                            | 0.282738                            | -0.4                      |
| BIESC-3L | 0.70320                           | 0.0049                          | 0.70320                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESD-1  | 0.70348                           | 0.0432                          | 0.70344                           | 0.512765                            | 0.512729                            | +3.3                      | 0.282748                            | 0.282747                            | -0.1                      |
| BIESD-1L | 0.70321                           | 0.0025                          | 0.70321                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESD-4  | 0.70425                           | 0.0285                          | 0.70423                           | 0.512776                            | 0.512739                            | +3.5                      |                                     |                                     |                           |
| BIESD-4L | 0.70323                           | 0.0040                          | 0.70323                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESE-1  | 0.70402                           | 0.0491                          | 0.70398                           | 0.512791                            | 0.512755                            | +3.8                      |                                     |                                     |                           |
| BIESE-1L | 0.70334                           | 0.0225                          | 0.70332                           |                                     |                                     |                           |                                     |                                     |                           |
| BIESE-2  | 0.70363                           | 0.1177                          | 0.70354                           | 0.512768                            | 0.512732                            | +3.4                      |                                     |                                     |                           |
| BIESE-2L | 0.70331                           | 0.0353                          | 0.70328                           |                                     |                                     |                           |                                     |                                     |                           |
| WAT-1    | 0.70421                           | 0.1461                          | 0.70409                           | 0.512680                            | 0.512643                            | +1.6                      | 0.282701                            | 0.282697                            | -1.8                      |
| WAT-1L   | 0.70353                           | 0.0111                          | 0.70353                           |                                     |                                     |                           |                                     |                                     |                           |
| WAT-2    | 0.70383                           | 0.1548                          | 0.70371                           | 0.512739                            | 0.512701                            | +2.8                      |                                     |                                     |                           |
| WAT-2L   | 0.70348                           | 0.0227                          | 0.70346                           |                                     |                                     |                           |                                     |                                     |                           |
| DSAT-2   | 0.70387                           | 0.0760                          | 0.70381                           | 0.512767                            | 0.512727                            | +3.3                      |                                     |                                     |                           |
| DSAT-2L  | 0.70332                           | 0.0340                          | 0.70329                           |                                     |                                     |                           |                                     |                                     |                           |
| DSAT-4   | 0.70358                           | 0.0867                          | 0.70351                           | 0.512766                            | 0.512728                            | +3.3                      | 0.282728                            | 0.282727                            | -0.8                      |
| DSAT-4L  | 0.70328                           | 0.0183                          | 0.70326                           |                                     |                                     |                           |                                     |                                     |                           |
| DIK-12   | 0.70341                           | 0.2060                          | 0.70325                           | 0.512779                            | 0.512739                            | +3.5                      |                                     |                                     |                           |
| DIK-12L  | 0.70322                           | 0.0029                          | 0.70322                           |                                     |                                     |                           |                                     |                                     |                           |
| DIK-13   | 0.70356                           | 0.2562                          | 0.70335                           | 0.512762                            | 0.512721                            | +3.2                      |                                     |                                     |                           |
| DIK-13L  | 0.70325                           | 0.0136                          | 0.70323                           |                                     |                                     |                           |                                     |                                     |                           |
| ZAND-1*  | 0.70353                           | 0.158                           | 0.70341                           |                                     |                                     |                           |                                     |                                     |                           |
| ZAND-4*  | 0.70355                           | 0.214                           | 0.70339                           | 0.512774a                           | 0.512735                            | +3.4                      | 0.282737                            | 0.282735                            | -0.5                      |
| ZAND-7*  | 0.703419                          | 0.179                           | 0.70328                           | 0.512771                            | 0.512735                            | +3.4                      | 0.282725                            | 0.282724                            | -0.9                      |

*Sample names with an "L" suffix indicate that the measurement was obtained on HCl-leached powders following the leaching procedure described by Mahoney (1987). The  $^{87}\text{Rb}/^{86}\text{Sr}$  values given were measured on the same leached and unleached sample aliquots used for Sr isotopic measurements. Nd and Hf isotope ratios were all obtained on unleached powders. Errors for  $^{87}\text{Sr}/^{86}\text{Sr}$  are less than 0.00002, those for  $^{143}\text{Nd}/^{144}\text{Nd}$  are less than 0.000012, and those for  $^{176}\text{Hf}/^{177}\text{Hf}$  are less than 0.000020, based upon both in-run and long-term uncertainties. The ratios of  $^{147}\text{Sm}/^{144}\text{Nd}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$  used for age-correction of Nd and Hf isotope ratios were calculated from the ICP-MS trace element concentration values given in Appendix E, Table 23. Epsilon values for Nd and Hf isotopes are calculated using the  $^{143}\text{Nd}/^{144}\text{Nd}$ ,  $^{147}\text{Sm}/^{144}\text{Nd}$ ,  $^{176}\text{Hf}/^{177}\text{Hf}$  and  $^{176}\text{Lu}/^{177}\text{Hf}$  values for CHUR from Bouvier et al. (2008) and an assumed age of 55 Myr for all samples. Data for Zandkopsdrift melilitites (\*) are from Ogungbuyi et al. (2022).*

**Appendix F: Table 25: Pb isotope compositions of Namaqualand melilitites.**

| Sample  | $^{206}\text{Pb}/^{204}\text{Pb}_m$ | $^{207}\text{Pb}/^{204}\text{Pb}_m$ | $^{208}\text{Pb}/^{204}\text{Pb}_m$ | $^{238}\text{U}/^{204}\text{Pb}$ | $^{232}\text{Th}/^{238}\text{U}$ | $^{206}\text{Pb}/^{204}\text{Pb}_i$ | $^{207}\text{Pb}/^{204}\text{Pb}_i$ | $^{208}\text{Pb}/^{204}\text{Pb}_i$ |
|---------|-------------------------------------|-------------------------------------|-------------------------------------|----------------------------------|----------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|
| LOU-3   | 25.918                              | 16.023                              | 40.864                              | 636.1                            | 0.5657                           | 20.368                              | 15.761                              | 39.865                              |
| LOU-4   | 23.818                              | 15.917                              | 40.152                              | 465.5                            | 0.5678                           | 19.757                              | 15.725                              | 39.418                              |
| BIESA-1 | 22.660                              | 15.866                              | 40.871                              | 241.8                            | 1.642                            | 20.551                              | 15.766                              | 39.770                              |
| BIESA-2 | 21.811                              | 15.818                              | 40.347                              | 252.1                            | 1.473                            | 19.612                              | 15.715                              | 39.317                              |
| BIESB-1 | 24.499                              | 15.956                              | 40.661                              | 407.8                            | 0.7370                           | 20.941                              | 15.789                              | 39.827                              |
| BIESB-3 | 22.173                              | 15.831                              | 40.194                              | 290.1                            | 0.7496                           | 19.641                              | 15.712                              | 39.590                              |
| BIESC-2 | 22.719                              | 15.873                              | 40.626                              | 184.8                            | 1.127                            | 21.107                              | 15.797                              | 40.048                              |
| BIESC-3 | 27.014                              | 16.066                              | 41.037                              | 684.1                            | 0.7035                           | 21.045                              | 15.784                              | 39.702                              |
| BIESD-1 | 24.495                              | 15.951                              | 40.045                              | 493.8                            | 0.4631                           | 20.186                              | 15.748                              | 39.410                              |
| BIESD-4 | 23.235                              | 15.890                              | 39.880                              | 365.2                            | 0.4660                           | 20.048                              | 15.739                              | 39.407                              |
| BIESE-1 | 24.212                              | 15.940                              | 41.156                              | 388.6                            | 1.213                            | 20.822                              | 15.781                              | 39.848                              |
| BIESE-2 | 21.961                              | 15.822                              | 39.981                              | 200.5                            | 1.076                            | 20.212                              | 15.740                              | 39.382                              |
| WAT-1   | 20.674                              | 15.773                              | 40.226                              | 145.2                            | 1.832                            | 19.407                              | 15.713                              | 39.489                              |
| WAT-2   | 21.099                              | 15.794                              | 40.888                              | 138.3                            | 1.933                            | 19.892                              | 15.737                              | 40.147                              |
| DSAT-2  | 21.525                              | 15.813                              | 40.044                              | 122.9                            | 0.9775                           | 20.452                              | 15.762                              | 39.711                              |
| DSAT-4  | 21.452                              | 15.808                              | 39.914                              | 226.5                            | 0.8765                           | 19.476                              | 15.715                              | 39.364                              |
| DIK-12  | 20.515                              | 15.766                              | 39.846                              | 73.65                            | 1.179                            | 19.873                              | 15.736                              | 39.605                              |
| DIK-13  | 22.038                              | 15.837                              | 40.393                              | 236.8                            | 1.176                            | 19.971                              | 15.740                              | 39.620                              |
| ZAND-4* | 20.588                              | 15.723                              | 39.435                              | 130.9                            | 1.207                            | 19.467                              | 15.671                              | 39.004                              |
| ZAND-7* | 21.726                              | 15.828                              | 40.157                              | 80.93                            | 0.9788                           | 21.032                              | 15.796                              | 39.941                              |

*All Pb isotope measurements were obtained on unleached powders.  $^{238}\text{U}/^{204}\text{Pb}$  and  $^{232}\text{Th}/^{238}\text{U}$  values are calculated from Pb, Th and U concentrations obtained by solution ICP-MS and reported in Table 23 (elemental and isotopic compositions were obtained on the same dissolved aliquots). Uncertainties for measured  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  isotope ratios are significantly less than 0.001, 0.001 and 0.002 based on in-run errors and long-term reproducibility. Uncertainties on age-corrected ratios are considerably larger than this because of the uncertainties on U, Th and Pb concentrations. In the worst-case scenario (which is for sample BIESC-3, which has the highest  $^{238}\text{U}/^{204}\text{Pb}$  and  $^{232}\text{Th}/^{238}\text{U}$  values), the uncertainty on age corrected  $^{206}\text{Pb}/^{204}\text{Pb}$ ,  $^{207}\text{Pb}/^{204}\text{Pb}$  and  $^{208}\text{Pb}/^{204}\text{Pb}$  values are 0.4, 0.2 and 0.9 given the  $\approx 5\%$  uncertainties on U, Th and Pb concentration determinations. In most cases, uncertainties on age-corrected Pb isotope values are significantly smaller than this. Data for Zandkopsdrift melilitites (\*) are from Ogungbuyi et al. (2022).*

## 10.7. Appendix G: Summary of electron microprobe standards.

Appendix G: Table 26: Summary of results for the measured electron microprobe standards.

| Abbreviation | Full name                      | Issuing organisation | SiO <sub>2</sub> | TiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Cr <sub>2</sub> O <sub>3</sub> | FeO   | MnO   | MgO   | CaO   | NiO   | Na <sub>2</sub> O | K <sub>2</sub> O | V <sub>2</sub> O <sub>5</sub> | Nb <sub>2</sub> O <sub>5</sub> | F     | Total    |
|--------------|--------------------------------|----------------------|------------------|------------------|--------------------------------|--------------------------------|-------|-------|-------|-------|-------|-------------------|------------------|-------------------------------|--------------------------------|-------|----------|
| CHRO         | 42NL11 chromite                | Carnegie Institution |                  | 0.47             | 19.41                          | 44.5                           | 22.1  | 0.21  | 12.3  |       | 0.14  |                   |                  | 0.25                          |                                |       | 99.38    |
| K-P          | Kakanui Pyrope NMNH143968      | Smithsonian          | 41.46            | 0.47             | 23.73                          |                                | 10.68 | 0.28  | 18.51 | 5.17  |       |                   |                  |                               |                                |       | 100.3    |
| K-H          | Kakanui Hornblende NMNH 143965 | Smithsonian          | 40.37            | 4.72             | 14.9                           |                                | 10.92 | 0.09  | 12.8  | 10.3  |       | 2.6               | 2.05             |                               |                                |       | 98.75    |
| RHOD         | Rhodonite                      | ??                   | 46.7             | 0.03             | 0.17                           |                                | 3.74  | 40.76 | 0.56  | 7.82  |       | 0.05              |                  |                               |                                |       | 99.83    |
| M-OL         | Marialahti olivine             | Smithsonian          | 40.24            |                  |                                |                                | 11.53 | 0.28  | 48.08 |       |       |                   |                  |                               |                                |       | 100.13   |
| JJGCPX       | JJG1424 cpx                    | UCT-XRF              | 54.57            | 0.27             | 3.03                           | 0.8                            | 1.65  | 0.05  | 16.44 | 21.45 |       | 1.43              |                  |                               |                                |       | 99.69    |
| JJGCPX       | JJG1424 cpx                    | UCT-EMP              | 54.57            | 0.23             | 2.96                           | 0.81                           | 1.62  | 0.07  | 16.78 | 21.63 |       | 1.67              |                  |                               |                                |       | 100.34   |
| JJGCPX       | JJG1424 cpx                    | Average*             | 54.57            | 0.25             | 3.00                           | 0.81                           | 1.64  | 0.06  | 16.61 | 21.54 |       | 1.55              |                  |                               |                                |       | 100.02   |
| AMPH         | Amphibole                      | UCT                  | 39.79            | 5.206            | 14                             | 0.018                          | 16.25 | 0.258 | 10.18 | 10.49 |       | 3.053             | 1.18             |                               |                                |       | 100.43   |
| ILMT         | Ilmenite                       | UCT                  |                  | 45.7             |                                |                                | 46.53 | 4.77  | 0.31  |       |       |                   |                  | 0.92                          |                                |       | 98.23 ** |
| RUT          | Rutile                         | UCT                  |                  | 100              |                                |                                |       |       |       |       |       |                   |                  |                               |                                |       | 100.00   |
| NISI         | high-nickel silicate           | Carnegie Institution | 28.69            |                  |                                |                                |       |       |       |       | 71.32 |                   |                  |                               |                                |       | 100.01   |
| FLUR***      | Fluorite                       | UCT                  |                  |                  |                                |                                |       |       |       | 51.33 |       |                   |                  |                               |                                | 48.67 | 100      |

### Comments:

\*This average value is the accepted value

\*\*Low total because all Fe reported as Fe<sub>2</sub>O<sub>3</sub> (actually contains 11.6 wt% Fe<sub>2</sub>O<sub>3</sub>, 36.1 wt% FeO)

\*\*\*Composition based on stoichiometry, wt.% Ca is given, NOT wt.% CaO