The relationship between dry granitoid magmatism and UHT-metamorphism

Bakhuis granulite belt, western Suriname

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Figures on title page:



a) The Kabalebo river just north of the Kabalebo-Zand Creek junction; **b)** mesoperthitic feldspar in a leucosome in the sillimanite gneiss (MKS 40). Darker grey blocky patches of alkali-feldspar exsolve from a plagioclase host; **c)** Misty Mountain as seen from the Kabalebo airstrip; **d)** two zircons from the Zand Creek zircon sample (MKS 36) with excellent examples of magmatic oscillatory and sector zoning.

Abstract

The Bakhuis granulite belt (western Suriname) consists of an early Proterozoic high-grade supracrustal sequence characterised by ubiquitous compositional banding. Orthopyroxene is invariably present in both the mafic and dominant quartzofeldspathic lithologies. Locally, the Bakhuis belt has experienced ultrahigh-temperature metamorphic conditions as indicated by the presence of sapphirine-quartz and orthopyroxene-sillimanite-quartz assemblages. In the SW of the belt, the granulites show an abrupt transition to a large $(30 \times 30 \text{ km})$ occurrence of orthopyroxene-bearing, hornblende-poor granitoid rocks (charnockites). These charnockites and their relation to the (UHT-) granulite metamorphism are the subject of this research project.

Petrography of the charnockites suggests high crystallisation temperatures, which is confirmed by ternary feldspar thermometry: between 940 and 990°C. The geochemical variation in the charnockite suite is explained by evolution of a parental charnockitic magma with ~65 wt% SiO₂ by fractional crystallisation of plagioclase, zircon, apatite and ilmenite. High concentrations of K₂O, P₂O₅, TiO₂ and Zr are typical of charnockites and reflect their unusual high-T melting conditions rather than a distinct source. Trace element data support charnockitic melt formation by partial melting of the intermediate, hornblende-poor UHT-granulites. Although the use of radiogenic isotopes is limited by the juvenility of the UHT-granulites, isotope data are in general agreement with the conclusion based on trace element data.

High-precision zircon U-Pb dating of 5 charnockite samples indicates that charnockite magmatism postdates granulite metamorphism by about 70 Myr. UHT-metamorphism has been dated at 2.07-2.05 Ga, while charnockite ages vary between 1959 and 1986 Ma. The three most reliable charnockite samples yield identical ages of 1980 Ma. Based on these ages, the hypothesis that charnockite magmatism and metamorphism occurred during a single protracted event, is rejected. The new geochronological and thermometric data obtained on the Bakhuis charnockites provide sound evidence for a second ultrahigh-temperature event in the central Guiana shield at 1.98 Ga.

Metadolerites and metagabbroic bodies that are common in the southwestern part are considered to play a crucial role in the development of the Bakhuis belt. It is argued that these mafic lithologies are related to mafic underplating synchronous with UHT-metamorphism at 2.07-2.05 Ga, acting as the dominant heat source. Delamination of the mafic slab and upwelling of hot, anhydrous asthenospheric mantle \sim 70 Myr later is the preferred explanation for the second ultrahigh-temperature event leading to partial melting of the granulites and charnockite generation.

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Chapter 1 - Introduction

1.1 Introduction

The Bakhuis belt is one of the granulite domains recognized within the central Guiana shield, South America. First considered to be part of a single "Central Guyana Granulite belt" (Kroonenberg, 1976), it is now accepted that the Bakhuis belt is unrelated to and unlike the other granulite domains; both the timing of metamorphism and peak metamorphic conditions are different (see section 2.2). The belt consists predominantly of intermediate and mafic high-grade supracrustal rocks, which are characterised by ubiquitous compositional banding at the cm to meter scale. Orthopyroxene is almost invariably present.

In the early 1970's, the exceptional high grade character of the granulites in the Bakhuis belt was first recognized by De Roever (*De Roever, 1975a,b*). The occurrence of assemblages of sillimanite-orthopyroxene-quartz and sapphirine-quartz point to metamorphic conditions in excess of 900 °C. These observations justify the recognition of the Bakhuis belt as an ultrahigh-temperature (UHT) domain (*De Roever et. al., 2003*). Moreover, the presence of orthopyroxene in leucosomes indicates migmatisation under granulite-facies conditions. Quantitative thermobarometry was first carried out by Karlijn de Groot for her MSc-thesis at the Vrije Universiteit (*De Groot, 2008*). Her results corroborated the petrographic indications that metamorphism occurred under UHT-conditions, reporting peak temperatures of 1000-1050 °C.

In the southwest, the granulites show a rather abrupt transition to orthopyroxene-bearing granitoids: charnockites *(see section 1.3)*. Although strikingly similar in mineralogy, these charnockites are distinguished from the metamorphic rocks by their truly magmatic textures and lack of compositional banding.

1.1.1 The Bakhuis charnockite-granulite connection

The pyroxene-bearing granitoids that are predominant in the southwestern part of the belt have been assumed to be genetically linked to the ultrahigh-temperature metamorphism and granulites. In the current hypothesis, the UHT-metamorphism was accompanied by partial melting; the charnockites represent these partial melts. This hypothesis was suggested because the granulites and the granitoid rocks occur in close contact within the same horst-like structure of the Bakhuis belt. While the belt itself is bounded by mylonitised shearzones, there is no evidence for any tectonic or structural discrepancies between the charnockites and granulites. Although the charnockites are predominant in the southwestern part of the belt, isolated occurrences are present in the northeastern part but are conspicuously lacking in the core of the Bakhuis horst. A detailed study of the field relationships between the two lithologies however, has never been carried out due to the poor level of bedrock exposure.

Additionally, the anhydrous, pyroxene-bearing nature of the charnockites indicates a high crystallisation temperature. This HT character is very unlike the other granitoid rocks found in the western Guiana shield. Therefore, a genetic link with the ultrahigh-temperature metamorphism appears more plausible than a relationship to the "normal" granites of the western Guiana shield.

As a final note, the fact that charnockites worldwide often occur within granulite zones (*Zhao et. al., 1997*) potentially points to a mutual origin. If, however, the charnockites prove not to be genetically related to the granulites but are merely intrusive in them, they might well have provided the heat necessary for metamorphism under conditions in excess of 950 °C.

The hypothesis that the charnockites in the Bakhuis belt represent partial melts of the granulites generated during the UHT-metamorphism, has never been examined in detail. This research project serves to investigate the relationship between the ultrahigh-temperature metamorphism and the dry granitoid magmatism in the Bakhuis belt. To evaluate the hypothesis stated above, a field campaign in the Bakhuis mountains was organised to explore the field relationships between the two lithologies in detail. Hampered by the poor level of exposure in a tropical rainforest, the field evidence might be inconclusive. Therefore, a detailed major and trace element analysis, in conjunction with a radiogenic isotope study, of both the granulites and charnockites is also carried out. A comparison of the geochemical signatures of the two lithologies could reveal if the granulites are indeed the source of the charnockitic melts. No Archaean protolith has ever been identified in the central Guiana shield. Despite previous assumptions of

an Archaean age for the Bakhuis belt, isotopic analyses of the granulites have revealed that they are derived from a juvenile source. Evidence for an inherited Archaean component is lacking *(De Roever et. al., 2003)*. New data acquired in this project will be used to assess the age of the charnockite protolith and the potential presence of Archaean material.

One crucial piece of evidence to test the hypothesis is the timing of the charnockite magmatism. Although the crystallisation age of the charnockites cannot prove or disprove a genetic link to the granulites, it can establish a relationship between the ultrahigh-temperature metamorphism and the magmatism. If the hypothesis were to be right and the UHT metamorphism was accompanied by partial melting, melting should be contemporaneous with the UHT-metamorphism. Hence, the crystallisation age of the charnockites should be equal to the age of peak metamorphic conditions. On the other hand, if the charnockites are not related to the UHT-event but are associated with the younger magmatic pulse that formed the "normal" granites of the Guiana shield, this should be reflected in the age as well.

The UHT-metamorphism is well constrained to have occurred between 2070 and 2050 Ma (De Roever et. al., 2003). The "normal" granites surrounding the Bakhuis belt are less precisely dated, but appear to have been emplaced well after the UHT-event from around 1980 to 1950 Ma (e.g. De Roever et. al., 2010 and in preparation). A more detailed discussion of the geochronology of the Bakhuis belt and surrounding lithologies is presented in chapter 2. The charnockites however, have not been properly dated. Zircon dating of a small charnockite occurrence in the north-eastern part of the belt yielded an age indistinguishable from the UHT-metamorphism (De Roever et. al., 2003). The main charnockite body in the SW has never been the subject of high-precision dating. Therefore, the scope of this project is also to put a firm age constraint on the charnockites in the Bakhuis belt. Zircon uranium-lead dating is a frequently used and most accurate tool to date magmatic rocks. Due to the high closing temperature of the U-Pb system in zircon, this method proves to be ideal for dating of the high-temperature granitoids.

1.1.2 Charnockites: petrogenetic considerations

Charnockites occur in a wide variety of structural settings and the diversity in field relationships suggests multiple modes of formation (*Bhattacharya, 2010*). The term charnockite has erroneously been used to describe orthopyroxene-bearing quartzofeldspathic granulites (see section 1.3), leading to a wealth of misunderstanding. Orthopyroxene in these "metamorphic charnockites" has in many cases been added metasomatically by CO₂ flushing: dehydration of hornblende to form opx (*Santosh and Omori, 2008*). Truly igneous charnockites on the other hand, form a common rock type that often occurs in high-grade metamorphic terrains (*Newton, 1992*). Furthermore, charnockites are regularly found in deep levels of large calc-alcalic batholiths (*Frost et. al., 2000*) and they constitute an important part of anorthosite-mangerite-charnockite-granite (AMCG) complexes (*Emslie, 1991; Duchesne and Wilmart, 1997*). They have common geochemical signature of high K₂O, P₂O₅ and TiO₂ that distinguishes them from orthopyroxene-bearing granulites and S-, I- and A-type granitoids. Coupled with the ubiquity of orthopyroxene and general absence of hornblende, this has led to the recognition of charnockites as a separate magma type different from other granitoid rocks (*Kilpatrick and Ellis, 1992*).

Perhaps impeded by the metamorphic versus magmatic debate, the origin and source of igneous charnockites are still uncertain. It is generally accepted that they represent intrusions of anhydrous magma into a dry crust, thereby potentially explaining the apparent symbiosis between charnockites and granulites. A wide variety of models has been proposed to explain charnockitic magmatism. Charnockites have been described as residues after the extraction of a granitic melt *(Hubbard, 1989)*. The amphibolite-granulite facies transition is characterised by breakdown of amphibole, often leading to dehydration melting. Resulting melts ascend and crystallise to form hydrous (i.e. hornblende-bearing), incompatible element enriched I-type granites. In this model, the water-deficient, melt depleted residue is considered to be charnockitic. Obviously, this model does not necessarily imply an igneous origin for these residual charnockites since the protolith could very well be for instance metasedimentary. However appropriate this model might be to describe specific occurrences of orthopyroxene-bearing quartzofeldspathic rocks, it fails to meet one of the prerequisites for charnockites: namely a per definition igneous origin. An adaptation of the residue model is the cumulate model, which is popular in explaining the presence of charnockites in AMCG-suites *(Emslie, 1991; Duchesne and Wilmart, 1997)*. Here, charnockites are treated as cumulates of fractional crystallisation processes of an already anhydrous parent magma.

As mentioned above, breakdown of amphibole often leads to dehydration melting and the production of I-type granites. Kar et. al. however propose that dehydration melting could also produce charnockitic melts and they claim that a large charnockite body in the Eastern Ghats granulite belt, India, is produced in this way *(Kar et. al., 2003; Kar and Bhattacharya, 2010).*

Another model related to dehydration melting is the residual source model *(Sheraton and Black, 1988; Munksgaard et. al., 1992).* This model explains charnockite magmatism by second-stage melting of previously melt-depleted granulitic lower crust. After dehydration melting and I-type granite extraction, this depleted, anhydrous residue is melted for a second time. The source granulites being dehydrated, the water-deficient fingerprint should be inherited by this second-stage melt. An obvious consequence of this model is that the second melt should not only be anhydrous, but also incompatible element depleted. If however, dehydration at the amphibolite-granulite facies transition occurs but does not initiate melting, no melt will be extracted and the residue will retain its magmaphile elements. If melting of these

no melt will be extracted and the residue will retain its magmaphile elements. If melting of these granulites eventually does occur, the resulting melt should be anhydrous but rich in incompatible elements. Such anhydrous but fertile granulites are considered to be a good candidate for the charnockite source rock (e.g. *Kilpatrick and Ellis, 1992; Zhao et. al., 1997*). The anhydrous but fertile granulites could represent either crustal rocks or mafic underplates, or a combination of the two.

As a means of dehydrating amphibolites without triggering the onset of wet melting, CO_2 flushing is often proposed *(Santosh and Omori, 2008)*. While the presence of even small amounts of water shifts the solidus of granitoid rocks to drastically lower temperatures, carbon dioxide only slightly lowers the solidus temperature. High proportions of CO_2 in the total fluid budget dilute the water-content and hence lower the H₂O-activity. Therefore, the influence water has on lowering the solidus is mitigated by the presence of carbon dioxide *(Winter, 2001)*. In extreme cases were large quantities of CO_2 are degassed from the mantle and enter the lower crust, the H₂O-activity could be sufficiently reduced to inhibit dehydration melting.

All the abovementioned models assume a predominantly crustal source for the generation of charnockites. Several authors however have opted the possibility that charnockites are the products of very prolonged fractional crystallisation of mantle derived melts. Fractional crystallisation of primitive mafic melts is one of the most important processes through which magmas evolve *(Winter, 2001)*. The extraction of mafic mineral phases such as olivine, clinopyroxene and plagioclase causes the remaining melt fractionation will therefore drive the melt to more siliceous compositions. It is therefore possible to generate a melt with a felsic composition (70 wt% SiO₂) by fractional crystallisation alone as witnessed by the volumetrically small occurrences of granitic rocks at mid-ocean ridges. In these cases, the granitic rocks represent the last bit of melt remaining after 98-99% fractional crystallisation. A prerequisite for this model is the efficient separation of fractionated phases from the remaining melt to prevent the crystals back-reacting with the melt. The process of prolonged fractional crystallisation is proposed to be able to generate rocks of charnockitic composition (e.g. *Mikhalsky et. al., 2006*).

As is evident from the preceding section, a myriad of potential models can be found in the literature relating to the source and mode of generation of charnockitic melts. The Bakhuis charnockites form a pristine example of igneous charnockites as they appear not to have been affected by subsequent high-grade metamorphism and largely retain their original magmatic textures. Therefore, the Bakhuis charnockites have the potential to elucidate the debate on the origin of charnockitic melts.

Hence, the second aim of this research project is to evaluate how the Bakhuis charnockites relate to other charnockites and attempt to constrain their mode of formation. Whole rock major and trace element data will be used to establish whether the Bakhuis samples are geochemically similar to the typical "charnockite magma type" (*Kilpatrick and Ellis, 1992*). Subsequently, the abovementioned models can be critically evaluated in the light of the new Bakhuis data.

1.1.3 The origin of UHT-metamorphism

Crustal metamorphism at temperatures exceeding 900 °C has not become generally accepted until the mid 1990's. Until then, a large part of the scientific community believed that granulite facies metamorphism took place at temperatures rarely exceeding 850 °C. Higher temperatures were considered to be insignificant anomalous outliers. Improvements in thermodynamical modelling and the recognition of the widespread occurrence of (U)HT granulite terrains *(Harley, 1998; see figure 1.1a)* led

to the growing awareness that metamorphic conditions could exceed 900 °C and that these conditions are common. An important cause of the slow acceptance of of UHT-metamorphism is the scarcity of diagnostic mineral assemblages. The most conspicuous assemblages can only develop in Mg-Al rich lithologies that are volumetrically rare in nature *(Kelsey, 2008).*



Figure 1.1 – **a)** occurrences of UHT metamorphism in the world. Note that the Bakhuis belt has not been included in this 2008 review. After Kelsey, 2008

b) temporal distribution of UHT metamorphism. After Kelsey, 2008 (adapted from Brown, 2006)

Ultrahigh-temperature crustal metamorphism is defined to occur in excess of 900 °C at a pressure limit corresponding to a geothermal gradient of >>20 °C km⁻¹ (Harley, 1998; Brown, 2006). The upper limit of UHTmetamorphism is formed by the liquidus of the rocks (Brown, 2007). A quick glance at these limits immediately raises two fundamental questions: i) why do crustal rocks not melt at these temperatures, and ii) what process can provide the heat required for such a high geothermal gradient?

The first of these questions is perhaps easiest to answer. Most crustal melting occurs under hydrous conditions. As already discussed in section 1.1.2, the presence of H_2O can drastically lower the solidus of rocks by up to 400 °C. Minimum eutectic granite melts can be generated at temperatures as low as 600 °C even when only a small amount of water is present.

The majority of intracrustal melting is related to convergent plate boundaries, that is in subduction zone settings, which are therefore the main sites of continental crust formation. Melt generation in subduction

zones is characterised by hydration of the mantle wedge by fluids escaping from the subducting slab, which causes wet partial melting *(Winter, 2001)*. This hydrous signature is subsequently inherited by any related melts forming the bulk of the continental crust. In this light, it appears high unlikely that crustal rocks can survive temperatures above 900 °C without melting. However, when the activity of water is suppressed (e.g. by the presence of large quantities of CO_2), the solidus of the rocks is shifted to significantly higher temperatures. During prograde metamorphism, dehydration reactions (e.g. the breakdown of muscovite or hornblende) often trigger wet partial melting. If carbon dioxide is abundant, it can sufficiently mitigate the influence of H_2O and prevent dehydration melting. Thus, water can effectively be driven off during prograde metamorphism without triggering wet partial melting, but this does require the involvement of large quantities of CO_2 .

The second question is subject to much more debate. Brown compiled data on the occurrence of granulite facies metamorphism throughout the history of the Earth and made an interesting observation (Brown, 2006; 2007). As can be seen in figure 1.1b, the occurrence of granulite metamorphism appears to be constrained to four distinct periods at around 2.6, 1.9, 1.1 and 0.5 Ga. These periods coincide with the supercontinent cycle of formation, suggesting a potential causal relationship between episodes of continental assembly and increased geothermal gradients. Before attempting to explain this apparent relationship, it is imperative to first establish the tectonic setting and heat source of ultrahigh-temperature metamorphism. General consensus is that it is impossible to generate UHT metamorphic rocks in a normal collisional setting (Collins, 2002). Numerical modelling has not been able to reproduce temperatures above 900 °C at relatively shallow depths (30-50 km), only the keels of thickened orogenies can just about reach these temperatures. Even elevating crustal heat production can not account for the anomalously high geothermal gradient (Kelsey, 2008). An accretionary setting has been proposed as a more likely candidate (e.g. Brown, 2006). During subduction of oceanic lithosphere, slab pull forces often lead to extension in the overriding plate and the development of backarc basins. The backarc is characterised by a high geothermal gradient that can be sufficient to explain shallow granulite facies

metamorphism. However, almost all granulite terrains show copious evidence for compressional stress as witnessed for instance by the presence of isoclinal folds. Collins proposed a model to account for this apparent contradiction *(Collins, 2002)*. He argues that the backarc is the tectonic setting where granulite terrains are formed. Active extension in the backarc, caused by slab retreat, elevates the geothermal gradient leading to conditions sufficient for granulite facies metamorphism. Pauses in slab retreat can be induced by the subduction of oceanic plateaus or seamounts, leading to short periods of compression. These phases of compression result in dynamic metamorphism in the backarc and the development of the typical compressional textures in granulite terrains. This model provides a plausible explanation for the fact that (U)HT-granulites occur far more often in accretionary than in collisional settings *(Kelsey, 2008)*, but the apparent relation to the supercontinent cycle remains unanswered.

Very recently, an exiting new model has been suggested *(Santosh et. al., 2011)*, which evokes ridge subduction as a prime cause of UHT-metamorphism. Their model proposes that during the subduction of a mid-ocean ridge, hot asthenospheric mantle is placed against continental lithosphere. Subduction zones are normally characterised as a hydrous environment by dehydration of the water-bearing subducting slab and sediments. When a ridge is subducted however, a slab window (i.e. the divergent plate boundary) opens which is filled by upwelling of hot, anhydrous mantle. Due to the absence of water and abundance of CO_2 in this window, dry granulite UHT-metamorphism can take place during the period that the slab window is in contact with the overriding continental crust. Unfortunately, also this model fails to provide an explanation for the UHT-supercontinent connection.

In the case of the Bakhuis belt, little is known about the origin of the ultrahigh-temperature metamorphism. Newly acquired field and geochemical data from the previously sparsely investigated southwestern part of the belt could enhance the understanding of the origin of the belt. Moreover, the possible relationship between charnockitic magmatism and UHT-metamorphism could shed more light on the geodynamical context of the Bakhuis belt in specific and the fundamental questions surrounding UHT-metamorphism discussed above in general. A heat source for the metamorphism has never been recognised but is generally assumed to be mafic underplating. If for instance our hypothesis is wrong and the granulites and charnockites are unrelated, the charnockites could very well have provided the heat required for UHT-metamorphism.

The final aim of this research project is therefore to attempt to construct a geodynamical model for the origin of the Bakhuis belt. This model endeavours to integrate multiple aspects such as the protolith of the charnockites, the heat source for the UHT-metamorphism and a plate tectonic setting for the high-temperature metamorphism and magmatism.

1.1.4 Summary

To summarize, this research project focuses on two major themes related to the widespread occurrence of anhydrous, orthopyroxene-bearing granitoids (charnockites) in a Paleoproterozoic ultrahigh-temperature granulite belt (Bakhuis belt) in western Suriname. The first theme is the question of the local relationship between the magmatism and UHT-metamorphism. Our hypothesis is that UHT-metamorphism was transitional to partial melting, i.e. the charnockites are partial melts of the granulites that formed contemporaneously with the UHT-event. Newly obtained field and geochemical data in conjunction with zircon dating of the charnockites will be used to test this hypothesis.

The second theme consists of the more general issue of high-temperature anhydrous melting and ultrahigh-temperature metamorphism. The petrogenesis of charnockitic melts is still subject to much debate and multiple models have been proposed to explain melting under high temperature conditions. Also the heat source and tectonic setting for UHT-metamorphism are far from established. This project endeavours to answer some of these questions using the previously uninvestigated Bakhuis belt as an example. Moreover, I will attempt to unite the UHT-metamorphism and charnockitic magmatism in a single geodynamic model.

1.2 – Project framework and funding

This research project is carried out as part of the curriculum of the MSc-program Earth Sciences – Solid Earth at the Vrije Universiteit Amsterdam. The ES-SE program requires two separate research projects to be undertaken; this project constitutes the Research Project Solid Earth (course code 450200), which is valid for 27 ECTS. The field campaign was carried out in February 2010.

The project was supervised by Dr. Emond W.F. de Roever, guest lecturer at the Vrije Universiteit and formerly employed as exploration geologist at the Geological Survey of Suriname (GMD). Dr. Fraukje Brouwer and Prof. Dr. Gareth Davies of the Vrije Universiteit kindly offered to act as second supervisor and reviewer for this research project.

All sample processing and geochemical analyses except for the zircon U-Pb analyses were carried out in the geological technical and isotope geochemical laboratories of the Faculty of Earth and Life Sciences at the Vrije Universiteit Amsterdam. Laser ablation ICP-MS analyses of zircon for uranium-lead isotopic composition was performed at the Faculty of Geosciences at the Universiteit Utrecht.

Financial support for this project was provided foremost by the Faculty of Earth and Life Sciences of the Vrije Universiteit Amsterdam. The costs for all sample processing and geochemical analyses at the VU laboratories were covered for, plus an additional subsidy to aid in financing the field campaign.

Due to the remote location of the fieldwork area in the tropical rainforest of Suriname, transportation and accommodation expenses were high. Moreover, the necessity of hiring local guides and the shipment of 70 kg of sample material to the Netherlands only added to the tight budget.

Fortunately, the Stichting Dr. Schürmann Fonds and Stichting Molengraaff Fonds provided much appreciated financial support. Besides making the field campaign possible, the Stichting Dr. Schürmann Fonds also generously covered the costs for the zircon U-Pb analyses at the Universiteit Utrecht.

1.3 – Nomenclature

The term "charnockite" was first used at the start of the previous century to describe orthopyroxenebearing granites in India *(Holland, 1900).* The term quickly became controversial as it was also used to describe felsic granulites in which orthopyroxene was present. Moreover, for many samples it proved to be impossible to tell whether the orthopyroxene crystallised directly from a melt or if it was formed by subsequent alteration (e.g. CO_2 metasomatism). By the 1960's the term "charnockite" was used for any orthopyroxene bearing quartzofeldspatic rock, both igneous and metamorphic. It could also refer to a series of igneous rocks, the charnockite series *(Le Maitre, 1989)*, with obscure terms for individual rock types such as "opdalite" (opx-bearing granodiorite) and "mangerite" (opx-bearing monzonite). This lead to a wealth of misunderstanding and terminological imprecision.

For the sake of clarity, in this thesis I will follow the nomenclature recommended by Frost and Frost *(Frost and Frost, 2008).* The term "charnockite" will be used in the broad sense to denominate any igneous, orthopyroxene-bearing granitoid rock. For a specific rock type, the prefix "opx-" will be used rather than the unfamiliar and old-fashioned terms from Le Maitre *(1989).* For example, an orthopyroxene-bearing tonalite will be referred to as "opx-tonalite" instead of "enderbite".

Chapter 2 - Geological setting

2.1 – Bakhuis Granulite belt

The Bakhuis mountains in western Suriname are the topographical expression of a high-grade granulite belt: the Bakhuis belt. The belt is dome-shaped but at present incorporated in a horst-like structure, approximately 30-40 km wide and 100 km long with a northeast-southwest orientation. It is bounded on both sides by steep, mylonitised shearzones. Rb-Sr and K-Ar isotopic systems in micas indicate formation of these shearzones at 1200 ± 100 Ma (*Priem et. al., 1971*) along pre-existing zones of weakness. Deformation during this Nickerie metamorphic event and subsequent re-activation during the Tertiary gave the belt its present-day shape, although formation of the belt may have initiated already during the last stage of the Transamazonian orogeny at ~2.05 Ga (*Delor et. al., 2003*). The horst-like structure of the Bakhuis belt is reflected in a continuous, steeply dipping foliation in both mafic and felsic minerals that follows the outline of the belt. Pelitic lenses also have the tendency to be aligned with the belt outline (*see figure 2.4*).

2.1.1 Metamorphic suite

As already mentioned in the introduction, the Bakhuis belt consist of high-grade mafic to intermediate metamorphic rocks of the Falawatra Group *(De Roever, 1975a,b)*. Conspicuous and ubiquitous compositional banding at the cm to meter scale argues for a predominantly metasedimentary or metavolcanic nature of the granulites *(see figure 2.1a, b, c)*. This is supported by the presence of intercalated pelitic gneiss, sillimanite quartzite, spessartine quartzite and calc-silicate bands, all of which



Figure 2.1 – **a)** preferential weathering displays compositional banding in the granulites, rock hammer (40 cm) for scale; **b)** compositional banding at cm scale, rock hammer for scale; **c)** felsic and more mafic band, coin for scale; **d)** tight folding in the granulites (photo reproduced by courtesy of E. de Roever). All photographs taken at the Blanche Marie Falls, Bakhuis Mountains, Suriname

have an undisputedly sedimentary origin *(De Roever et. al., 2003).* These lithologies however, are rare and form a subordinate part of the granulite belt. Banded quartzofeldspathic rocks make up about 50-55% of the metamorphic suite. They are almost invariably orthopyroxene-bearing and contain no to little alkali- feldspar. Fine and coarse grained pyroxene-bearing amphibolites constitute approximately 35% of the belt and occur both as discrete bands up to a meter in thickness and as massive units. The remaining 10-15% is made up of the before-mentioned pelitic gneisses and similar lithologies and felsic leucosomes. Isoclinal to tight folding is developed in the banded rocks and boudinage of the mafic bands is common *(see figure 2.1d).*

The exceptional high-grade character of the Bakhuis belt is demonstrated by the widespread occurrence of orthopyroxene-bearing leucosomes, indicating that migmatisation occurred under anhydrous granulitefacies conditions. Already in the 1970's, high-grade mineral assemblages of orthopyroxene-sillimanitequartz and sapphirine-quartz were recognized (De Roever, 1975a,b). After the general acceptance of ultrahigh-temperature metamorphism, new petrological and geochemical data have proven that the Bakhuis belt has at least locally experienced UHT-conditions (De Roever et. al., 2003). Figure 2.4 displays three localities where evidence for ultrahigh-temperature metamorphism has been found. The two asterisks in the SW part of the belt depict the presence of UHT-remnants such as a post peaktemperature assemblage of sapphirine-cordierite symplectites adjacent to coarse sillimanite. The locality in the northeastern part of the belt (see figure 2.4) has an unambiguous UHT character. In metapelites, sapphirine has been found, in cases in direct contact with quartz: a prime indicator for UHT-conditions (Harley, 2008). Moreover, UHT-conditions are indicated by the orthopyroxene-sillimanite-quartz assemblage and the presence of aluminous orthopyroxene containing >8 wt% Al₂O₃ (De Roever et. al., 2003). Petrological evidence points towards a counter clockwise pressure-temperature path characterised by almost isobaric cooling (see figure 2.2). An early assemblage of cordierite + sillimanite (I) is replaced by the peak-T assemblage sapphirine + quartz (II). Upon initiation of cooling, peak metamorphic conditions are represented by the assemblage orthopyroxene-sillimanite-quartz (III). Such a PT-path is often interpreted as being the result of magmatic underplating (e.g. Wells, 1980). This conclusion is also reached by De Roever et. al., who invoke juvenile, hot mafic magma as the heat source for the UHTmetamorphism (De Roever et. al., 2003; Delor et. al., 2003). Substantial amounts of Fe₂O₃ incorporated in sillimanite, sapphirine and orthopyroxene in conjunction with the common occurrence of spinel point to a high oxygen fugacity (De Roever et. al., 2003).



Figure 2.2 – pressure-temperature diagram for high fO₂ metapelites in KFMASH, displaying the counter clockwise PT-path for the ultrahightemperature metamorphic rocks in the northeastern Bakhuis belt. Figure after De Roever et. al., 2003

Quantitative geobarothermometry was carried out by Karlijn de Groot for her MSC-thesis. New samples were taken in and around the previously investigated UHT-occurrence. Peak PT-conditions were concluded to have been 950-1050 °C at a pressure of 1.1 GPa (*De Groot, 2008*). However, hampered by the high $f O_2$ and extensive post-metamorphic re-equilibration this peak pressure is most likely an overestimate. The garnet-orthopyroxene pair used as a barometer was not in equilibrium, leading to an erroneously high pressure (*De Roever, pers. comm.*). A previous estimate of 850-900 MPa (*De Roever et. al., 2003*) provides a better constraint on peak pressure conditions. The peak temperature is less ambiguous since it was confirmed by the ternary feldspar thermometer, which is independent of $f O_2$ and unaffected by post-metamorphic re-equilibration (*De Groot, 2008*).

The ultrahigh-temperature metamorphic event in the Bakhuis belt has been dated using the Pbevaporation method on zircon (*De Roever et. al., 2003*). Zircons from a garnet-sillimanite gneiss yielded an age of 2072 ± 4 Ma and a garnet gneiss was dated at 2055 ± 3 Ma. A pegmatitic layer within the garnet gneiss provided scattered ages between 2081 and 2058 Ma. The older ages from this sample were interpreted to represent an inherited component. An enderbitic gneiss also gave highly scattered ages ranging from 2153-2086 Ma, again being interpreted as a dominantly inherited Pb-component. Predominantly based on the garnet-sillimanite and garnet gneiss samples, it was concluded that the UHTmetamorphism occurred between 2072 and 2050 Ma (*De Roever et. al., 2003*). These ages have been confirmed by a SHRIMP analysis of another enderbitic gneiss (2052 ± 15 Ma). Additionally, the garnetsillimanite gneiss was analysed by both SHRIMP and SIMS (2072 ± 16 and 2067 ± 9 Ma respectively), which again corroborated the previously mentioned ages (*J.M. Lafon, unpublished confidential data*).

2.1.2 Other lithologies

The main objective of this research project is to investigate the relationship between the metamorphic suite discussed in the previous section and a large occurrence of igneous charnockites in the southwestern part of the belt. As discussed in the introduction, it is hypothesised that the charnockites formed contemporaneously to the UHT-event. A small charnockite occurrence in the northeast of the belt has been dated by zircon Pb-evaporation at 2065 ± 2 Ma (*De Roever et. al., 2003*). High-precision dating of the main charnockite body is needed to critically asses the hypothesis. Abundant gabbroic to ultramafic occurrences are also present in the SW part of the belt, together with scattered lenses of pelitic gneiss. Based on field relationships and occurrences outside the Bakhuis belt, these (ultra)mafic intrusions of the so-called De Goeje type are considered to be considerably younger than the UHT-metamorphism and charnockitic magmatism (*Delor et. al., 2003*).

A characteristic feature of the Bakhuis belt is the omnipresence of metadolerite dikes. They consist of fine-grained pyroxene-amphibolite. Although the dikes are usually straight and discordant, they are in some cases slightly deformed *(see figure 2.3)*, suggesting synkinematic emplacement. Zircon Pb-evaporation ages of 2056 ± 4 Ma and 2060 ± 4 Ma for a metadolerite dike *(De Roever et. al., 2003)* confirmed the synkinematic character. Since these dikes are not found in other granulite belts in the region, they are considered typical for the Bakhuis belt.

An anorthosite body measuring 3 by 4 km was discovered in the core of the Bakhuis Mountains. The intrusion is partly massive and partly layered. Zircon Pb-evaporation dating yielded an age of 1980 ± 5 Ma for the anorthosite (*De Roever et. al., 2003*).



Figure 2.3 – **a)** straight metadolerite dike, pencil for scale; **b)** slightly folded, synkinematic metadolerite dike (photo reproduced by courtesy of E. de Roever); Both photographs taken at the Blanche Marie Falls, Bakhuis Mountains, Suriname

2.2 – Regional geology of western Suriname

The Bakhuis belt is not the only granulite domain within the central part of the Guiana shield. Highgrade rocks also occur in the Cauarane-Coeroeni belt (previously named Central Guiana Granulite belt): an arcuate domain that extends eastwards for 1000km from the Cauarane belt (*Fraga et. al., 2008*) in Roraima State (Brazil) via the Kanuku horst in southern Guyana to the Coeroeni gneiss in SW Suriname (*Kroonenberg and De Roever, 2009; see figure 2.7*). At first is was believed that the Kanuku horst connected to the Bakhuis belt (*Kroonenberg, 1976*), but the lack of relief between the two horsts and aeromagnetic evidence (*Hood and Tyl, 1973*) do not support this continuation. As is explained below, the Bakhuis belt is a completely separate entity within the central Guiana shield, both in lithology as well as in age.

The Coeroeni gneiss in Suriname differs markedly from the Bakhuis horst in multiple aspects (Kroonenberg, 1976). Contrary to the Bakhuis granulites, the Coeroeni gneiss contains only minor amounts of amphibolites and chiefly comprises quartzofeldspathic paragneiss and sillimanite gneiss. The rocks have been metamorphosed at amphibolite to granulite facies and show intense folding and migmatisation. The metamorphism however, is lower-grade than in the Bakhuis mountains, with PT-conditions just exceeding 800 °C (Kroonenberg, 1976). Moreover, the characteristic metadolerite dikes of the Bakhuis belt are not present in the Coeroeni gneisses. The first attempt to date metamorphism in the Coeroeni area was not very successful. A Rb-Sr isochron on a selection of drill core samples yielded an age of 2001 ± 97 Ma (Priem et. al., 1977). Recent zircon Pb-evaporation dating of a leucosome gave a poorly constrained age of 1991 ± 25 Ma for the Coeroeni migmatisation. Surprisingly, two zircons with Archaean Pb-evaporation ages were found in a cordierite-tonalite gneiss (De Roever et. al., 2010). The two ages of 2.72 and 2.89 Ga suggest the involvement of an inherited Archaean component, metamorphism in the Coeroeni gneiss is significantly younger than the Bakhuis UHT-metamorphism.

The Cauarane-Coeroeni belt continues westward from the Coeroeni gneiss to the Kanuku horst in Guyana and Cauarane belt Roraima, Brazil. The Kanuku horst and Cauarane belt are much less well documented than the Bakhuis horst and Coeroeni gneiss. They consist of amphibolite to granulite facies ortho and paragneisses together with abundant migmatites (*Delor et. al., 2003*). Neodymium model ages of ~2.2 Ga point to a juvenile protolith (*Ben Othman et. al., 1984*). The timing of metamorphism has been constrained by a single monazite SHRIMP age of a synkinematic granite in the Cauarane belt: 1995 \pm 4 Ma (*Fraga et. al., 2008*), which is in excellent agreement with the 1991 Ma age for the Coeroeni metamorphism.

Surrounding the Bakhuis belt is a large zone of plutono-volcanic felsic rocks, referred to as the "normal" granites in the introduction, named the Uatumã supergroup (Delor et. al., 2003). This zone is located in between the TTG-greenstone belt to the north (see section 2.3) and the Cauarane-Coeroeni belt to the south and extends from central Suriname westwards to Roraima State (Brazil) and eastern Venezuela (see figure 2.7). In Suriname, the Uatumã supergroup consists of two generations of granitoid rocks (Delor et. al., 2003). An extensive area of felsic to intermediate metavolcanic rocks occurs in western Suriname. These rocks underwent low-grade metamorphism, are characterised by wide, open folding and have a partly ignimbritic origin. The metavolcanics are considered to be comagmatic with intrusive, hypabyssal leucogranites, granophyric and fine-grained granites. These lithologies are also prominent in Guyana, Venezuela and Roraima. Zircon U-Pb dating by SHRIMP has revealed that the Surumu group in Roraima, which is equivalent to the metavolcanics, has an age between 1.99 and 1.96 Ga (Reis et. al., 2000). This age is supported by recent Pb-evaporation dating of zircons from the metavolcanics and a hypabyssal granite from Sipaliwini (southern Suriname) that yielded 1987±4 Ma and 1980±4 Ma respectively (De Roever et. al., 2010). A second generation of granitoid magmatism is formed by biotite granites, which are intrusive in the metavolcanics and associated hypabyssal granites and contain xenoliths of these lithologies (Delor et. al., 2003). Hence, the biotite granites undoubtedly postdate the metavolcanics, which is confirmed by a 1949±12 Ma zircon age (De Roever et. al., in preparation). It is assumed (Kroonenberg and De Roever, 2009) that certain granitic rocks from Brazil are equivalent to the biotite granite in Suriname. These have been dated at 1.97-1.93 Ga (e.g. Santos et. al., 2004; Almeida et. al., 2007).



Figure 2.4 – simplified geological map of the Bakhuis horst and surrounding area. Note the location of the UHToccurrence in the NE and the two UHT-remnants denoted with an asterisk in the SW of the belt. After De Roever et. al., 2003

The similarity in ages between the metavolcanics and biotite granites indicates a protracted magmatic event generating a large amount of granitoid rocks. The few neodymium model ages determined for Uatumã granitoids (*Lamarão et. al., 2005; De Roever et. al., 2010*) all point to a juvenile character (T_{DM} of ~2.3-2.1 Ga) and hence a period of major crustal growth.

As is evident from the preceding section, the Bakhuis belt is highly dissimilar to the other geological units in western Suriname. The UHT-metamorphic character typical of the Bakhuis belt is not witnessed in the Cauarane-Coeroeni belt and there are marked differences in lithology. Moreover, metamorphism in this belt postdates UHT-metamorphism by at least 50 Myr. An obvious relationship between the Bakhuis belt and surrounding Uatumã granites is neither easily supported since again a 70-100 Myr age difference is present.

2.3 – Guiana Shield

The Guiana shield is a predominantly Paleoproterozoic part of the Amazonian Craton in South America. It constitutes the northern part of this craton; the southern domain is named the Brazil Central shield. The two shields are separated by the Amazon trough, a basin created during the Paleozoic related to the break-up of Gondwana *(see figure 2.5)*. Although the Amazon trough is completely covered by recent sediments and bedrock outcrops are non-existent, it is believed that the main geological units of the Guiana shield continue underneath the trough without offset *(e.g. Kroonenberg and De Roever, 2009)*. The Amazonian Craton was part of Gondwana and, before the opening of the Atlantic Ocean, it was connected to the cratons in West Africa *(Zhao et. al., 2002)*.



Figure 2.5 – *location of the Amazonian Craton in South America*

The Guiana shield covers most of northeastern South America, ranging from eastern Venezuela via Guyana and Suriname to French Guiana in the east. It also includes the part of Brazil north of the Amazon river. The western boundary is formed by the Andean orogenic chain *(Kroonenberg and De Roever, 2009)*, its northeastern limit is the oceanic crust of the Atlantic Ocean. Due to the location in equatorial regions and inherent inaccessibility and tropical weathering, the Guiana shield is one of the least investigated Precambrian terrains in the world.

For such a large shield, its main period of formation spans only ~300 Myr during the Transamazonian orogeny in the Paleoproterozoic. Two Archaean terrains have been recognized within the shield *(see figure 2.7)*. In the far west, the Venezuelan Imataca complex is characterised by Transamazonian reworking of a Archaean (2.6-3.7 Ga) protolith *(e.g. Tassinari et. al., 2003)*. On the eastern side of the shield, preserved Archaean nuclei occur in the states of Amapá and Para, Brazil. Pb-Pb dating has revealed several late Archaean gneisses with Nd model ages up to 3.3 Ga *(e.g. Rosa Costa et. al., 2003)*. Interestingly, in this area evidence has been found for Transamazonian granulite metamorphism in conjunction with charnockitic magmatism, dated at 2.07-2.06 Ga. This forms a striking resemblance to the Bakhuis belt *(Rosa Costa et. al., 2003)*.

Between these two Archaean domains, the Guiana shield is made up of Paleoproterozoic crust that shows a progressive younging towards the SW *(Delor et. al., 2003; see figure 2.7)*. This crust was produced as a direct consequence of the collision between the West African shield and Amazonian craton during the so-called Transamazonian orogeny. There is very little evidence for a pre-Transamazonian craton to the south of the Guiana shield apart from the relatively small Amapá and Para complexes.

The oldest Proterozoic rocks in the eastern part of the Guiana shield are the "Île de Cayenne" gabbro and trondhjemites in French Guiana, which are dated at 2216±4 Ma (Milesi et. al., 1995). These rocks are considered to be juvenile tholeiitic melts emplaced in a mid-ocean ridge or backarc setting, representing a stage of plate divergence. Besides this small occurrence of ocean ridge tholeiites, the northern part of the Guiana shield consist of a major greenstone belt that can be traced for 1000 km. It is broken in two in the centre by the Bakhuis horst and bounded on the sides by the Imataca and Amapa Archaean domains. The belt comprises submarine lavas and pyroclastic rocks interbedded with arcderived sedimentary layers. Closely associated with the greenstone belt is a plutonic tonalite-trondjemitegranodiorite (TTG) suite. Together, they form the north Guiana TTG-greenstone belt. Radiometric dating has shown that the TTG-greenstone belt was formed between 2.18 and 2.13 Ga and positive intial $\varepsilon_{\rm Nd}$ values preclude the involvement of pre-Transamazonian crust (Delor et. al., 2003). The only exception is the Archaean fingerprint of a metapelite interbedded in the greenstones that has a negative initial ε_{Nd} value. This metapelite is presumable derived from the poorly specified Amazonian craton to the south (see figure 2.6). The TTG-greenstone belt is formed as a result of N-S convergence between the West African shield and the Amazonian craton. Southward subduction of the newly-formed oceanic crust led to TTG-magmatism and the formation of an island-arc.

At approximately 2.10 Ga, the direction of compression changed from N-S to NE-SW. This led to pronounced E-W sinistral shearing in conjunction with subordinate conjugate dextral shear. As a result, small pull-apart basins opened, which were subsequently filled with detrital sandstones and conglomerates derived from the TTG-greenstone belt. This detrital unit is famous for its gold-bearing strata in Suriname and French Guiana. Another effect of the change in compression direction was partial melting and migmatisation of the TTG-complexes. The resulting suite of granitoid rocks is dated at 2.11-2.08 Ga (*Delor et. al., 2003*) and makes up a large part of French Guiana and eastern Suriname (*see figure 2.7*). This migmatisation of the TTG-suite marked the end of the main phase of the Transamazonian orogeny, the final suturing between the West African shield and Amazonian craton and the birth of the Guiana shield.

The subsequent event to affect the Guiana shield was the ultrahigh-temperature metamorphism in the Bakhuis belt at 2.07-2.05 Ga described in section 2.1, followed by the metamorphism in the Cauarane-Coeroeni belt and the Uatumã magmatism at 1.99-1.93 Ma *(see section 2.2).* Together, these form the late Transamazonian phase. As already mentioned earlier, the TTG-greenstone belt is broken in half by the Bakhuis horst. On a continental scale, the two branches of the belt display a pinch and swell structure, narrowing towards the Bakhuis horst and Imataca and Amapa domains *(see figure 2.7).* Delor et. al. propose that this continental scale boudinage is a direct result of the sinistral shearing of the TTG-greenstone crust at 2.07-2.05 Ga *(Delor et. al., 2003).* They argue that extension and crustal stretching as a response to late Transamazonian oblique plate convergence led to mantle upwelling and UHT-metamorphism in the Bakhuis belt *(see figure 2.6).*



Figure 2.6 – Geodynamic model for the Paleoproterozoic evolution of the Guiana shield. After Delor et. al., 2003





Figure 2.7 – Geological map of the Guiana shield. After Delor et. al., 2003

After the late Transamazonian phase, magmatic activity subsided in the eastern part and the epicentre moved progressively to the southwest. In Roraima state (Brazil), magmatism continued with charnockitic magmatism at 1.94-1.93 Ga (*Fraga et. al., 2009*) and occurred fairly continuous up to 1.87 Ga (*Santos et. al., 2003*). Other notable post-Transamazonian magmatism includes anorogenic granites and related major tin deposits near Manaus (Brazil) and the Avanavero pigeonite dolerite dikes and sills. The latter are widespread in the Guiana shield and also occur in and near the Bakhuis belt. Baddeleyite from Avanavero sills have been dated at 1782 ± 3 Ma (*Santos et. al., 2003*).

Thick sequences of siliciclastic sediments derived from the Transamazonian belt (the Roraima supergroup) cover parts of the Guiana shield. These essentially flat-lying sediments were deposited around 1.87 Ga as constrained by interbedded pyroclastic layers *(Santos et. al., 2003)* and form plateaus in Venezuela (the Angel Falls for instance), Guyana and Suriname (Tafelberg in central Suriname).

In the Mesoproterozoic, the western half of Suriname and Guyana underwent a metamorphic event that resulted in resetting of Rb-Sr and K-Ar isotopic systems in micas. This Nickerie metamorphic episode (also known as the K'Mudku event) activated the shear zones along the Bakhuis dome giving it its horst-like shape (*De Roever et. al., 2003*). It did however, not result in magmatism or high-grade metamorphism. The Nickerie event was dated at 1200 ± 100 Ma (*Priem et. al., 1971*).

The Guiana shield and West African craton remained a single block until the Phanerozoic opening of the Atlantic Ocean. The craton was separated along the northern margin of the TTG-greenstone belt. The extension caused by the divergence of the African and South American plates is witnessed by the occurrence of N-S orientated dike swarms in the Guiana shield: the Apatoe dolerites.

Chapter 3 – Methodology

3.1 – Sampling strategy

During the field campaign, systematic sampling of the Bakhuis mountains was impossible due to the very poor level of exposure and lack of infrastructure. Outcrops are very sparse in the dense forest. Soil formation is highly efficient in the moist and hot conditions of equatorial regions and soils can reach thicknesses of up to 20 meters. Moreover, due to the Proterozoic age of the Bakhuis mountains, most of the relief is flattened out by erosion and mountains are covered by the regolith. Only deeply incised rivers and streams have the potential to expose the bedrock. Most outcrops are therefore located in riverbeds, large rapids in the rivers and small waterfalls. Misty Mountain appears to be the only exception; "normal" outcrops do occur on the slopes and top of this mountain.

Due to this poor level of exposure, it is very difficult to establish a clear understanding of field relationships; it is almost impossible to asses how two outcrops only 200m apart are linked to each other. Moreover, the proximity to the western boundary and shear zone of the horst and hence the high degree of mylonitisation also adversely affect the possibility of understanding the bedrock geology. Despite these problems, excellent outcrops are present in the Kabalebo river, Zandcreek, Misty Mountain and Blanche Marie area *(see figure 4.1 for a map of the research area and sampling locations)*. Representative samples are taken from these locations. In the case of river outcrops, samples were taken as high above the water level as possible to minimise the amount of time the rocks have been submersed in the river recently. Weathered parts of the outcrops were avoided and only visually unaltered rocks were samples. Additionally, pristine samples of the metamorphic suite are derived from a drill core (LA 156) from the centre of the Bakhuis belt.

Emphasis was placed on sampling the igneous charnockitic suite and representative metamorphic lithologies, but mafic rock types (e.g. dolerites, meta-dolerites etc.) occurring in the Kabalebo area were also samples for petrography. In total, 21 samples were taken from the igneous charnockite suite for petrographic and geochemical analysis (all for major and minor elements with XRF, a selection of 10 samples for trace elements and isotopes with ICP-MS and TIMS respectively). Five of the charnockite samples were selected in the field for zircon U-Pb geochronology and trace element study. The zircon samples were significantly larger, about 6-8 kg, compared to the normal sample size (1-2 kg). From the Kabalebo area, two mafic lithologies were also sampled for geochemical analysis (major and trace elements, isotopes) and an additional 10 for petrography only. The northernmost sample from the Kabalebo area is a sillimanite gneiss that is part of the metamorphic suite. Next to the sillimanite gneiss, 9 metamorphic samples were taken from the Blanch Marie area. Together with 6 samples from drill core LA 156, this adds up to 16 samples from the metamorphic suite. All of these are again processed for petrography and major and minor element analysis; 9 have been selected for trace elements and isotopes.

3.2 – Whole rock preparation

3.2.1 Coarse processing

All 39 samples that were selected for geochemical analysis were processed at the Geological Technical Laboratory and Mineral Separation Laboratory at the VU Amsterdam. Whole rock samples were cut into inch-sized blocks using a diamond blade saw. Care was taken to remove weathering rims and altered parts. One or two small rectangular pieces per sample would provide a thin section, which were prepared at the Geological Technical Laboratory. The remaining pieces were passed through a steel jawcrusher to crush the sample to a gravel. Before every sample, the jawcrusher was cleaned meticulously using a steel brush, ethanol and compressed air. A representative ~ 100 g split was taken to provide a whole rock powder. For the five samples selected for zircon U-Pb dating and trace element analysis, the remaining gravel was processed further in the Mineral Separation Laboratory *(see section 3.4.1)*; for the other samples, the gravel was set aside. The whole rock split was subsequently powdered in an agate ring mill (1 min.) and agate planetary ball mill (60 min.). This powdering procedure ensures effective powdering and homogenisation of the samples while keeping contamination to a minimum. All agate parts were cleaned after every use by running them with clean quartz sand and water, followed by a thorough wash with demineralised water and ethanol.

3.2.2 XRF preparation

For XRF analysis, both a fused glass bead (used for major element concentration analysis) and a pressed powder pellet (for minor elements) were prepared. About 15 g of whole rock powder was dried in clean glass vials in a stove overnight and stored in a dehumidifier afterwards.

For the pressed powder pellets, 4.500 grams of dried sample powder was carefully mixed with 0.450 g of an organic binder (EMU 120 FD). The mixture was transferred to a small aluminium cup and loaded in an X-press pneumatic press. Samples were pelletized at a pressure of 20 tons for 30 seconds, after which pressure was gradually released. For very felsic samples with a silica-content >70 wt%, producing a pressed pellet might be problematic since these tend not to bind successfully. Upon release of pressure, small flakes may come off the pellet leading to an irregular surface. Five pellets continued to have minor flaking even after multiple attempts. These samples are analysed with imperfect pellets, potentially leading to a higher measurement uncertainty. To rule out the possibility of flakes coming off in the XRF and thereby potentially damaging the X-ray tube, these pellets were vigorously blown with compressed air and put in a vacuum stove overnight.

Analysis of the fused glass beads requires not only a dry sample powder, but also complete removal of lattice-bound volatiles such as OH-groups, carbon and sulphur. Therefore, >1g of dried sample powder was ignited in ceramic crucibles in an oven at 1000 °C for 30 minutes. Samples were carefully weighed before and after ignition. The change in mass is the loss on ignition (LOI) and is taken to represent the wt% of volatiles in the sample. Care must be taken however when using these data, since the oxidation of iron to Fe₂O₃ incorporates oxygen from the air into the sample, thereby adding weight. All samples have very low LOI, on average 0.2 wt% and all below 0.5 wt%. Two samples have negative LOI, indicating that oxidation of iron is indeed having an effect.

Once cooled down, 1.000 g of ignited sample powder was carefully mixed with 4.000 g of Spectroflux 110. This is a mixture of lithium-tetraborate and lithium-metaborate that serves to drastically lower the melting temperature of the sample powder enabling fusion of the bead at a reasonable temperature. The sample was subsequently loaded into a clean platinum (95% Pt, 5% Au) crucible and fused in a Philips PerlX3 machine at \sim 1150 °C. The glass was cast in a platinum casting dish and allowed to cool. In case the bead broke during cooling, the fusion process could be repeated straight away using the broken bead. The platinum crucibles and casting dishes were cleaned at the start of the sample series for 24 hours in 2% HF to remove any glass droplets. In between samples, they were cleaned in an ultrasonic bath in 20% citric acid.

3.2.3 Sample digestion

Both ICP-MS analysis and chromatographic separation for isotope composition analysis require a fully dissolved sample. Conventional dissolution of silicate rocks relies on concentrated hydrofluoric acid (HF) to break down silica bonds in the sample. However, some minerals such as rutile, garnet and most importantly zircon, fail to break down (completely) at room pressure. When complete dissolution of these phases is required, the only fully successful approach is using Parr-bombs *(Mahlen et. al., 2008).* In this method, the samples are placed in steel-jacketed Teflon vessels in an oven for multiple days, leading to a sufficiently high temperature and pressure to break down the silica bonds in zircon. Since zircon is a common accessory phase in the charnockites *(see chapter 4),* it was decided to dissolve all samples using the Parr-bombs. Moreover, the use of the Parr-bombs keeps the option open for Lu-Hf isotope analysis since zircon includes most of the hafnium present in the sample.

Besides the 21 samples selected for ICP-MS and isotope analysis, two basaltic USGS reference materials (BHVO-2 and BCR-2) were included in the sample series to serve as external standards. These standards underwent the same Parr-bomb digestion procedure as the samples. An additional BCR-2 standard was also included. This standard was dissolved using the regular hotplate destruction procedure and served as a check for the Parr-bomb destruction method. Since the BCR-2 basalt is considered to be zircon-free, the two digestion methods should yield identical results.

All dissolution and chromatographic separation procedures were performed in the clean lab at the VU Amsterdam. This filtered air over-pressured clean lab ensures very low air particle levels (200-400 particles/m³) and low blank concentrations. All labware used during the procedures was cleaned

meticulously with double distilled 6-7N HCl for >3 days, again ensuring very low blank levels for all elements of interest. For all samples and standards, 80-100 mg of whole rock powder was carefully weighed out and put in polytetrafluorethylene (PTFE) Teflon[®] bombs. Double distilled concentrated hydrofluoric acid (3 ml) and nitric acid (1 ml) were added to the samples. The Teflon bombs were sealed and mounted in steel-jacketed Parr-bombs. They were placed in an oven at 200 °C and left for five days. Upon cooling down, the solutions were transferred to clean 30 ml perfluoralkoxy (PFA) Savillex[®] beakers with the aid of 6-7M HCl. The samples were dried down at 130 °C and nitrated twice with 15-20 drops concentrated HNO₃ to break down insoluble chloride- and fluoride salts. When completely dry, the samples were taken up in 10 ml 3.0N HNO₃.

For the hotplate digestion standard, 80-100 mg of BCR-2 standard powder was put in a clean 30 ml PFA Savillex[®] beaker together with 3 ml concentrated HF and 1 ml concentrated HNO₃. The beaker was closed tightly and put on a hotplate at 140 °C for 3 days. Subsequently, the solution was dried down, nitrated twice and taken up in 10 ml 3.0M HNO₃. From here on, it was treated in exactly the same way as the other samples.

An aliquot corresponding to 1 mg of original sample powder was taken from the total solution for ICP-MS analysis. This aliquot was diluted 4000-5000 times with 5% HNO_3 in a 10 ml centrifuge tube. Exact dilution factors were calculated by weighing after every step. Before analysis on the ICP-MS, the samples were homogenised and centrifuged for 10 minutes at 4000 rpm.

3.2.4 Whole-rock Sr separation procedure

All samples analysed for trace element concentrations on the ICP-MS were also prepared for strontium and neodymium *(see next section)* isotope composition analysis. Strontium chromatographic separation was performed using 0.08 ml quartz columns loaded with Eichrom[®] Sr-spec resin. The columns were rinsed with three alternations of 10 column volumes $3.0M \text{ HNO}_3$ and water and subsequently conditioned with 5 column volumes $3.0M \text{ HNO}_3$. Samples were equilibrated overnight on a hotplate at 120 °C and ultrasoned for 1 hour before centrifuging for 5 minutes at 4000 rpm. An aliquot corresponding to 500 ng strontium was loaded onto the columns. The matrix was rinsed off with 30 column volumes $3.0M \text{ HNO}_3$ and the Sr-fractions were eluted with 10 column volumes water.

One drop of 0.5% phosphoric acid (H_3PO_4) was added to the strontium fractions before they were dried down overnight. Phosphoric acid serves to facilitate loading of the samples for TIMS analysis and does not form a significant contribution to the blank. Once dry, the samples were nitrated twice with 2-3 drops of concentrated nitric acid to remove any organic material (the ion-exchange resin) present in the fractions. After nitration, samples were ready for TIMS analysis.

3.2.5 Whole rock Nd separation procedure

Chromatographic separation of neodymium from the matrix was achieved with a double column procedure in which light rare earth elements are first separated from the matrix using TRU-spec columns and neodymium is subsequently separated from the other LREE with LN-spec columns. For neodymium isotope analysis on a thermal ionisation mass spectrometer *(TIMS, see section 3.3.4)*, complete separation of Nd from samarium is required because of isobaric interference of ¹⁴⁴Sm on ¹⁴⁴Nd. Although an interference correction can be applied by monitoring ¹⁴⁷Sm, dissimilar mass-dependant fractionation in the ion source of the TIMS for the two elements introduces a large error in this correction. The conventional method for separation of Nd from Sm at the VU Amsterdam made use of HDEHP-columns. While these columns are fully effective and no samarium is present in the neodymium fractions, the very fine HDEHP resin leads to a low column flow rate: a series of ten samples takes three days. Besides being time consuming for large sample series, the low flow rate also potentially leads to increased blank values.

A new method for Nd-Sm separation using LN-resin was recently developed at the VU Amsterdam by Richard Smeets. Previous attempts with LN-resin were unsuccessful and small amounts of samarium in the neodymium fraction could not be prevented. In theory, using very fine LN-resin and columns with a high height to width ratio should result in effective separation *(Richard Smeets, pers. comm.)*. The Nd-

fraction of these columns should have a high neodymium yield (> 90%), contain no samarium and little cerium and praseodymium. Moreover, the flow rate of these columns would be sufficiently high that the entire procedure can be performed on two instead of three work days. As a pilot study, two LN-columns were made and calibrated with the ICP-MS. Subsequently, they were tested using well constrained geostandards.

Preliminary results obtained on two USGS reference materials were promising. Neodmymium in marine mud MAG-1 and Hawaiian basalt BHVO-2 was separated using the new LN-columns and analysed on the TIMS. Both standards yielded pure neodymium fractions with low concentrations of cerium and praseodymium. Samarium was very effectively separated from the LREE and completely absent from the Nd-fraction. Isotopic compositions measured by on the TIMS were in excellent agreement with both the in-house long-term average and published values (e.g. *Weis et. al., 2006*).

Due to the positive results for the two standards, it was decided to implement the new LN-spec column procedure as staple for neodymium isotope composition analysis at the VU. The samples of this research project are the first to be processed according to the new procedure and serve as a final test case. As an additional check, two random columns were calibrated and their yield was determined *(see below)*. Moreover, four samples were randomly selected to be duplicated using the conventional HDEHP-columns to check the reproducibility and precision of the new LN-columns,

3.2.5.1 TRU-columns

Light to middle REE (lanthanum to gadolinium) can be efficiently separated from the sample matrix using Eichrom[®] TRU-resin. This resin was loaded onto 0.3ml quartz columns, which were subsequently rinsed with twice alternating 10 column volumes 2.0M HNO₃ and H₂O and conditioned with 1ml 2.0M HNO₃. After the Sr-column procedure, total solutions for all samples were dried down and taken up again in 5-7 ml 2.0M HNO₃. The solutions were left to equilibrate on a hotplate at 120 °C the night prior to column extractions. The next day, they were ultrasoned for 1 hour, homogenised and centrifuged for 5 minutes at 4000rpm before loading onto the columns. An aliquot corresponding to 600ng neodymium was loaded for all samples, except for 5 samples with a very low Nd-concentration. For these samples, only 300ng was loaded. A larger aliquot of 1200 ng was used for the four samples duplicated with the HDEHP columns; these samples were split in two equal aliquots after elution of the REE-fraction.

The matrix consisting of, amongst others, the heavy rare earth and major elements was washed off with 25 column volumes 2.0M HNO₃ before elution of the light REE with 10 column volumes H_2O . The REE-fraction was dried down on a hotplate at 120 °C overnight and subsequently taken up in 1ml 0.165M HCl for both the HDEHP and new LN-columns.

3.2.5.2 LN and HDEHP-columns

Two random, new-made LN-columns were calibrated and tested for their yield using a 100ppb reference solution containing cerium, neodymium and samarium. An aliquot corresponding to 1 μ g Ce, Nd and Sm of the reference solution was passed through the columns. Every 1ml of the eluate covering the entire pre-fraction, Nd-fraction and Sm-fraction was collected and analysed on the ICP-MS for concentrations. The pre-fraction was eluted with 0.165M HCl, the subsequent Nd-fraction with 0.30M HCl and finally the Sm-fraction with 0.50M HCl. The ICP-MS results were normalised to a calibration curve derived from 1 and 100ppb solutions of the same reference solution. The results of the column calibration and yield test are displayed in figure 3.1.

The results of the present column calibration are in perfect accordance with the preliminary calibration performed by Richard Smeets. The position of the elemental peaks had not drifted and the separation between samarium and neodymium is very effective. Yields for all elements were very close to 100% and hence it can be safely assumed that no sample is lost on the columns. The overlap between the cerium and neodymium peaks indicates that Ce-free Nd-fractions can not be obtained and a compromise has to be made. Based on this calibration, it was decided to shift the end of the pre-fraction back by 0.5 ml to 10.5 ml 0.165M HCl. This leads to a neodymium yield of 90-95%, with a minor addition of cerium (< 10%). Considering the high yield and complete absence of Sm, the results are highly satisfactory and the columns are taken into common use.



Figure 3.1 – results of the column calibration and yield test obtained with the ICP-MS: the percentage of total sample per ml of eluant. Note the very effective separation of Sm but the overlap of the Ce and Nd fractions.

The LN-columns are fixed, meaning that the same resin is used multiple times. This implies that the columns require meticulous cleaning before every use to prevent memory effects of previous samples *(see table 3.1)*. The columns were cleaned with consecutive 4 ml 6M HNO₃, 2M HF, H₂O and 6-7M HCl. Subsequently, the columns were rinsed with ~1 ml 0.165M HCl and stored overnight in vials containing clean ~0.1M HCl.

The next day, the columns were cleaned once more with 4 ml 6-7M HCl and 4 ml H_2O before conditioning with 2 ml 0.165M HCl. The REE-fractions were left to equilibrate on a hotplate at 120 °C overnight, ultrasoned for 1 hour and transferred to pre-cleaned 1.5 ml centrifuge tubes. Just prior to loading, the samples were centrifuged for 4 minutes at 12,000 rpm. Of the 1 ml sample solution, 950µl was loaded to prevent bringing any residue (e.g. organics from the TRU-columns) onto the columns. The pre-fraction was eluted with 9.5 ml 0.165M HCl, after which the neodymium fraction was collected with 4 ml 0.30M HCl. Before storage, the columns were cleaned with 4 ml 6-7M HCl and 1 ml 0.165M HCl to remove i.a. the samarium fraction.

Four samples for Nd-isotope composition analysis were duplicated using the conventional HDEHPcolumns. Similar to the new LN-columns, the HDEHP-columns are fixed and can be used multiple times before the resin needs to be changed. A column extraction requires three consecutive days for the HDEHP-columns. On the first day, the columns were cleaned with two alternations of 3ml 6M HNO₃ and H₂O. Afterwards, 30ml 6-7M HCl was loaded onto the columns, they were covered with parafilm and left overnight. The TRU-spec REE-fractions were put on a hotplate at 120 °C to equilibrate. The next day, cleaning continued with $3ml H_2O$, $6M HNO_3$ and again H_2O . Subsequently, the columns were conditioned with 3ml 0.165M HCl. The REE-fractions were ultrasoned for 1 hour, homogenised and transferred to pre-cleaned 1.5 ml centrifuge tubes. The samples were centrifuged for 4 minutes at 12,000 rpm before loading 95% of the 1ml solution onto the columns. To ensure that the sample was washed into the resinbed, four times four drops of 0.165M HCl were dropped onto the lower, convex part of the column reservoirs. Afterwards, the remainder of the pre-fraction eluate was added at once. The prefraction volume was calibrated for every column individually and ranged between 12 and 16 ml 0.165M HCl. The columns were again covered with parafilm and the pre-fraction passed through overnight. On the third and last day, the Nd-fraction was eluted with 4ml 0.30M HCl. Before storage, the columns were cleaned with 3-5ml 6-7M HCl and conditioned with ~1ml 0.165M HCl.

A drop of 0.5% phosphoric acid was added to the neodymium fractions from both column extractions before dying down. The samples were nitrated twice with concentrated nitric acid. Subsequently, they were ready for analysis on the TIMS.

Step	eluent	volume [ml]	comment	Table 3.
Cleaning	6M HNO₃	4		Sm-fractic
Cleaning	2M HF	4		for Sn
Cleaning	H ₂ O	4		out whe
Cleaning	6-7M HCI	4		compositio
Conditioning	0.165M HCI	1	store overnight	desired.
Cleaning	6-7M HCI	2		
Cleaning	H ₂ O	4		
Conditioning	0.165M HCI	1		
Sample loading	0.165M HCI	1		
Pre-fraction	0.165M HCI	9.5		
Nd-fraction	0.30M HCI	4	collect fraction	
Sm-fraction	0.50M HCI	5	collect fraction	
Washing	6-7M HCI	4		
Conditioning	0.165M HCI	1	store	

Table 3.1 – elution schemefor the new LN-columns. TheSm-fraction is only applicablefor Sm-isotope dilutionmeasurements and can be leftout when only Nd-isotopecomposition analysis isdesired.

3.3 – Whole rock analyses

3.3.1 XRF analysis

Major and minor element concentrations were determined on pressed powder pellets and fused glass beads *(see section 3.2.2)* using a Philips Pananalytical MagiXPro X-ray Fluorescence (XRF) spectrometer at the VU Amsterdam. For both pellets and beads, measured, interference corrected spectra intensities were converted to concentrations against a calibration curve. This curve consists of 30 natural standards with highly variable compositions and is updated every 6 months.

Glass beads were measured at an acceleration voltage of 40 kV and beam current of 90 mA. Measured elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, Ba, P) are expressed as weight percent of the oxides. Iron is reported as ferric (Fe₂O₃) since it is presumed to be completely oxidised during ignition *(see section 3.2.2)*. As this may not represent the true ferric/ferrous iron ratio of the sample prior to ignition and to facilitate comparison to other data, Fe₂O₃ is normalised to total ferrous iron: FeO*. Pressed powder pellets were measured at 60 kV and 60 mA for a small selection of trace elements including Rb, Sr, Y, Zr, V, Cr and Pb.

During each measurement session, four USGS reference materials (AGV-1, GSP-1, BHVO-2 and BCR-2) are included as "unknown" standards to check the precision of the calibration curve and monitor long-term drift. Figure 3.2 displays replicate analyses of these standards measured over the last 6 years. As is evident from this figure, strontium, zirconium and vanadium concentrations vary little over time and deviate less than 1% from the long-term average. The same holds for rubidium, except for the BHVO-2 reference material, which shows significantly more scatter. This might be related to the relatively low concentration of this element in the BHVO-2 standard *(see table 3.2).* Chromium shows much more scatter; individual measurements of BCR-2 regularly deviate more than 20% from the mean. This is again potentially caused by low Cr-concentrations in the standards.

Table 3.2 shows a summary of the long-term averages of both major and minor elements for the reference materials. Selected major elements (Si, Fe, Mg, K) generally deviate less than 2% from either the long-term mean and recommended values. Minor elements show more variation with an apparent negative correlation to the elemental concentration. As was already noted in figure 3.2, rubidium is in excellent agreement with recommended values for AGV-1, GSP-1 and BCR-2 that have Rb-concentrations >50 ppm, but shows considerably more scatter for BHVO-2 (\sim 9 ppm Rb). Vanadium shows a similar trend of increasing error with decreasing concentration.



Figure 3.2 (previous page) – Deviations from the average for Sr, Rb, Zr, V and Cr concentrations as measured with the XRF on pressed powder pellets of four USGS reference materials over the last 6 years. Chromium is not included in the BCR-2 graph since scatter exceeded 50%. The last three analyses are measured at the same time as the samples from this research project.

	SiO ₂	Fe ₂ O ₃	MgO	K₂O	Sr	Rb	Zr	v	Cr
AGV-1	Majors	(n = 51)			SPEL (n	= 71)		VCCBS	(n = 70)
Average [wt%, ppm]	59.62	6.76	1.46	2.96	655.69	68.19	226.90	120.72	9.43
Standard deviation 2σ	0.40	0.07	0.02	0.02	2.78	0.47	2.71	1.47	1.30
RSD (%) 2σ	0.67	1.11	1.12	0.59	0.42	0.69	1.19	1.22	13.77
Deviation from recomm. (%)	1.33	-0.14	-4.79	1.38	-0.95	1.32	-0.05	0.60	-5.74
GSP-1	Majors	(n = 49)			SPEL (n	= 70)		VCCBS (n = 67)	
Average [wt%, ppm]	67.04	4.21	0.92	5.49	232.04	256.80	505.26	49.69	11.19
Standard deviation 2σ	0.89	0.05	0.02	0.07	1.00	0.99	2.61	1.19	1.36
RSD (%) 2σ	1.33	1.26	2.65	1.25	0.43	0.39	0.52	2.40	12.16
Deviation from recomm. (%)	-0.27	-1.88	-4.18	-0.31	-0.84	1.10	-4.67	-6.25	-13.95
BHVO-2	Majors	(n = 50)			SPEL (n = 70)			VCCBS (n = 68)	
Average [wt%, ppm]	48.90	12.09	7.03	0.51	396.61	9.27	170.59	317.44	294.74
Standard deviation 2σ	0.68	0.20	0.15	0.01	2.14	0.40	2.54	4.14	8.19
RSD (%) 2σ	1.39	1.65	2.12	1.42	0.54	4.37	1.49	1.31	2.78
Deviation from recomm. (%)	-1.44	-1.16	-2.15	-0.51	1.96	-5.38	-0.82	0.14	5.27
BCR-2	Majors	(n = 50)			SPEL (n	= 71)		VCCBS	(n = 68)
Average [wt%, ppm]	53.45	13.56	3.47	1.76	348.08	49.46	188.47	406.74	14.58
Standard deviation 2σ	0.76	0.19	0.08	0.02	1.42	0.35	2.09	3.57	8.48
RSD (%) 2σ	1.43	1.43	2.44	1.37	0.41	0.71	1.11	0.88	58.14
Deviation from recomm. (%)	-1.20	-1.75	-3.38	-1.64	0.60	3.05	0.25	-2.23	-19.01

Table 3.2 – reproducibility of a selection of major and minor elements as measured with the XRF over the last six years.

Assessment of the reproducibility of rubidium and strontium is of critical importance since the XRF data for these elements will be used for age correction of Sr isotope ratios. Propagated errors on the Rb/Sr ratio compared to USGS recommended values are around 1.5% for AGV-1 and GSP-1, 3.1% for BCR-2 and 5.7% for BHVO-2. Hence, a realistic error on a XRF-determined Rb/Sr ratio is 3%. The fact however that reproducibility of the Rb-concentration measurements drastically deteriorates at low rubidium contents might be problematic. Some of the samples can be expected to have a low rubidium concentration (<10 ppm), potentially, leading to (much) larger errors on the Rb/Sr ratio used for age correction (see BHVO-2 standard in table 3.2).

3.3.2 ICP-MS analysis

Trace element analysis of 21 samples was performed using a single-collector quadrapole Thermo X-Series II inductively coupled plasma mass spectrometer (ICP-MS) at the VU Amsterdam. The procedure at the VU uses a BHVO-2 solution with an accurately known concentration and composition as an internal standard. This solution is measured at the start of the sample series and is subsequently used to convert measured counts to concentrations for all samples, using BHVO-2 trace element concentrations from i.a. Raczek et. al. *(2001)*. An additional BHVO-2 solution is measured every 4-7 samples to correct for drift of the ICP-MS instrument during the measurement session. Several tune solutions are analysed at the start of each sample series, which were used to correct for isobaric interferences.



Figure 3.3 – Deviations from the average for Rb, Sr, Zr, Nd, Sm and Hf concentrations measured with the ICP-MS for the BCR-2 USGS reference material over the past 5 years. The standards included in the samples series for this project have been measured on January 12th, 2011.

Three external standards were included in the sample series *(see section 3.2.3)* and these were measured as unknowns. A blank was also added to check for potential contamination during sample digestion or ICP-MS measurement. The ICP-MS measurement session was characterised by significant instrumental drift during the analyses as is witnessed by the systematic difference between BCR-2 standards measured at the start and end of the sample series *(see section 3.3.3)*. Table 3.3 summarises the long term performance of the ICP-MS as monitored by regular analyses of the BCR-2 standard. Average concentrations are in very good agreement with recommended values. However, reproducibility for most elements is only 10-15% and individual analyses can show a significant deviation from both the long-term average and recommended values *(see figure 3.3)*. The BCR-2 and BHVO-2 standards measured during the sample series from this research project deviate 5-10% form the average.

The large deviation of the BCR-2 and BHVO-2 could imply a significant error on the ICP-MS samarium/neodymium ratio used for age correction of isotope data. However, although the individual concentrations differ greatly from recommended values, the Sm/Nd ratio is much less affected and shows only minor deviance (<2%). Fulmer and Kruijer *(2009)* propose an error of 4% on ICP-MS determined Sm/Nd ratios when used for age correction. Several elements such as antimony, indium and bismuth show increased deviation and scatter for the replicate BCR-2 analyses. For certain elements (Sb) this is most likely caused by uncorrected isobaric interferences, for others (In, Bi), the very low concentration (<0.05ppm) straddles the detection limit leading to higher measurement errors. These elements have therefore been excluded from the results in appendix 2.4

BCR-2 (n = 137)	Rb	Sr	Zr	Ce	Nd	Sm	Hf
Average [ppm]	49,00	340,82	197,16	53,33	28,85	6,60	4,80
Standard deviation 2σ	8,30	44,89	25,87	6,62	3,54	0,81	0,62
RSD (%) 2σ	16,95	13,17	13,12	12,41	12,27	12,32	12,94
Deviation from recomm. (%)	4,48	0,24	4,87	0,81	0,53	0,51	0,02

Table 3.3 – reproducibility of a selection of trace elements in the BCR-2 USGS reference material measured with the ICP-MS over the past 5 years.

3.3.3 Comparison between XRF and ICP-MS results

Several minor and trace elements measured on pressed powder pellets on the XRF were duplicated with the ICP-MS. Figure 3.4b shows a comparison between the data obtained with the two analytical methods. As is evident, there is significant deviance for certain elements. High field strength elements such as zirconium and niobium have systematically higher concentrations in the ICP-MS measurements; an effect that has been noticed before *(Fulmer and Kruijer, 2009)*. Lead shows a comparable enrichment in the ICP-MS measurements. On the other hand, rubidium is scattered but does not have a consistent offset and XRF analyses of strontium and yttrium are in good agreement with ICP-MS data. An explanation for these inconsistencies is not easily found. The blank measurement incorporated in the ICP-MS sample series indicated that contamination was not an issue. In the case of zirconium, the four external standards included in the XRF analysis are generally in accordance with recommended values, except for the GSP-1 standard displayed a deviation from the recommended value of -4.67% *(see table 3.2)*, but this is not sufficient to explain the ~20% offset for Zr. Moreover, niobium shows similar higher ICP-MS concentrations but lacks a large deviation from recommended values for the XRF standards.

To evaluate whether the Parr-bomb (whole-bomb, WB) digestion method has an influence on the XRF versus ICP-MS discrepancy, a hotplate digested (HP) BCR-2 standard was included in the sample series. Trace element concentrations for both digestion methods were determined by ICP-MS. The BCR-2 basaltic reference material does not contain appreciable amounts of zircon, rutile, garnet or other notoriously hard to digest phases. Hence, results for the two digestion methods should be identical; any variation that is present is likely obtained during the whole-bomb destruction process.

Figure 3.4a shows a comparison between the whole-bomb and hotplate digested BCR-2 standards for a selection of trace elements. The WB standard is characterised by a fairly constant negative offset of ~5% relative to the HP method. A clear correlation between element type (e.g. high field strength elements) and deviance is not present. The large-ion lithophile elements display somewhat more scatter, an observation made as well by Fulmer and Kruijer (2009). Their data suggested that LILE are potentially "lost" during the WB procedure, reporting increased scatter and systematic deficiencies for rubidium in the WB-ICP-MS solutions relative to XRF data. These findings are not corroborated by the present results; the LILE do not show abnormal behaviour in figure 3.4a and ICP-MS data actually agree fairly well with XRF results (see figure 3.4b).

Based on the comparison for basaltic standards, it can be concluded that the systematic difference between the WB and HP digestion methods is likely caused by instrumental drift (the two standards were measured during two different sessions). The whole-bomb destruction procedure appears not to have a detectable effect on trace element concentrations. Care however must be taking when extrapolating this conclusion to felsic lithologies since the whole-bomb procedure influence might be masked by low trace element concentrations.

An explanation for the deviance between XRF and ICP-MS results exhibited by certain elements is probably related to instrumental drift of the ICP-MS instrument. As shown in section 3.3.1, XRF results for minor and trace elements with a concentration >20ppm in USGS reference materials are in excellent agreement with recommended values. For elements with concentrations below approximately 20ppm however, XRF errors and deviation from recommended values increase drastically. This could partly explain the apparent discrepancy between ICP-MS and XRF data: low concentration elements such as niobium and lead show more variance and deviation, while elements with higher concentrations (Rb, Sr, Y) are in much better agreement *(see figure 3.4b)*. Zirconium concentrations in the samples however, far



Figure 3.4 (previous page) – comparison between ICP-MS and XRF analytical techniques. **a)** trace element (ICP-MS) ratios of BCR-2 USGS reference material dissolved using the whole bomb technique over the hotplate procedure (see text for explanation); **b)** trace element concentrations measured by ICP-MS versus XRF

exceed 20ppm but nonetheless display large inconsistencies. Additional scatter and XRF versus ICP-MS deviation can be caused by instrumental drift of the ICP-MS *(see figure 3.4a)* and potentially uncorrected isobaric interferences. The latter may especially be true for zirconium, whose abnormal behaviour remains ill constrained.

As a general conclusion, the XRF provides high quality data for minor and trace elements with concentrations exceeding 20ppm. For these elements, XRF results are consistent through time and in good agreement with recommended values. For less concentrated elements, XRF data rapidly deteriorate and ICP-MS results are preferably used. Although the ICP-MS is characterised by increased instrumental drift and measurement errors are larger, detection limits are very low and allow analysis of concentrations <1ppm with a precision better than 10%.

3.3.4 Thermal Ionisation Mass Spectrometry (TIMS)

Strontium and neodymium isotope composition analyses were carried out using a MAT 262 RPQ+ thermal ionisation mass spectrometer (TIMS) at the VU Amsterdam. This TIMS instrument is equipped with 8 Faraday collectors (of which 6 have adjustable positions) and two secondary ion multipliers allowing for simultaneous measurement of multiple isotopes *(see table 3.4)*.

	jump	L2	L1	Centre	H1	H2	H3
Sr		⁸⁴ Sr	(⁸⁵ Rb)	⁸⁶ Sr		⁸⁷ Sr (⁸⁷ Rb)	⁸⁸ Sr
Nal	1	¹⁴² Nd (¹⁴² Ce)	¹⁴³ Nd	¹⁴⁴ Nd (¹⁴⁴ Sm)	¹⁴⁵ Nd	¹⁴⁶ Nd	(¹⁴⁷ Sm)
Nd	2	¹⁴³ Nd	¹⁴⁴ Nd (¹⁴⁴ Sm)	¹⁴⁵ Nd	¹⁴⁶ Nd	(¹⁴⁷ Sm)	¹⁴⁸ Nd (¹⁴⁸ Sm)

Table3.4–TIMSFaraday collector setup for
strontium and neodymium
measurements. Interfering
masses are depicted in
italics and between
brackets

3.3.4.1 Strontium

Strontium fractions were loaded onto pre-cleaned and outgassed single rhenium (annealed) filaments. First, the fractions were re-dissolved in 4-6 μ l 10% HNO₃. Half of this fraction was subsequently loaded, together with 2 μ l of a TaCl₅ activator. Loading only half of the sample allows for a possible re-analysis of the sample; the tantalum activator serves to facilitate efficient and stable evaporation of strontium in the ion source.

All samples were run in a static data collection mode, which has proven to be nearly as reproducible as dynamic mode for this instrument. A gain calibration was performed at least once every 3 samples to monitor drift in the amplifier gains. Potential drift in the magnetic field or acceleration voltage (10 kV) was regulated by performing a peak centre multiple times throughout a measurement.

The samples were slowly heated to about 1350 °C and subsequently the ion beam was focussed. The filament current was increased until the signal intensity of ⁸⁸Sr was in between 3 and 5 volts. Data were acquired in 7-12 blocks of 10 scans, with each scan having an integration time of 16 seconds. Every block ended with a baseline measurement and a peakcenter.

Mass-dependant isotope fractionation is the main source of error in TIMS analyses when it is not corrected for. The high temperature in the source of the TIMS favours ionisation of light isotopes over heavier ones. Light Sr-isotopes (⁸⁴Sr, ⁸⁶Sr) therefore show an anomalous enrichment at the start of a

measurement. With time, the light isotopes become depleted in the source and the signal becomes more enriched in heavier isotopes. Fortunately, this fractionation process can easily be corrected for. For heavy elements, the ratio of two non-radioactive, non-radiogenic isotopes must always be the same in nature and can therefore be used for normalisation. For strontium, samples are normalised to the natural ⁸⁶Sr/⁸⁸Sr ratio of 0.1194 using an exponential fractionation law *(Thirlwall, 1991)*.

Isobaric interference of ⁸⁷Rb on ⁸⁷Sr *(see table 3.2)* forms another source of error in strontium isotope composition analyses by TIMS. The chemistry procedure *(see section 3.2.4)* was very effective in separating rubidium from the strontium and very little Rb was present in the Sr-fractions. Due to its high volatility, any Rb still present in the sample could easily be removed by short thermal stressing of the filament. The contribution of rubidium to ⁸⁷Sr was therefore negligible for all samples. Nevertheless, isobaric interference was corrected for by monitoring ⁸⁵Rb and calculating ⁸⁷Rb (⁸⁷Rb/⁸⁵Rb = 0.3857). Although the rubidium ratio is not corrected for mass fractionation, the interference correction did not introduce a significant error.

The external precision or reproducibility of the sample series was checked by measuring the NBS 987 strontium standard at least once a day. The 8 replicate analyses measured during the sample series yield a constant offset to the canonical value of 0.710245 for the NBS 987 standard. This deviation is most likely caused by deterioration of the Faraday collectors with time rather than contamination of the NBS 987 standard solution. Standards measured in dynamic mode (when cup efficiency factors cancel out) are in good agreement with the proposed 0.710245, and other geostandards measured in static mode display the same offset to excepted values. All samples are therefore normalised to a value of 0.710245 for NBS 987. Once corrected, the BHVO-2 and BCR-2 standards are in perfect agreement with both the long-term average at the VU and proposed values *(Elburg et. al., 2005; Weis et. al., 2006; see figure 3.5e,f)*. This correction however, is very small compared to the observed range in ⁸⁷Sr/⁸⁶Sr ratios of the samples.

To check whether the whole-bomb digestion procedure had any effect on strontium isotope composition, the WB and hotplate digested BCR-2 standards were both analysed. Results were within error of each other *(see appendix 2.5 and figure 3.5d)* and in agreement with recommended values. There was no evidence at all that the WB-dissolution method imparted any influence on the Sr-IC.

3.3.4.2 Neodymium

Contrary to strontium, neodymium was measured in a double jump dynamic routine *(see table 3.4).* Using a dynamic routine, each isotope is measured in two different Faraday detectors. As a result, both cup efficiency and gain factors cancel out. Despite a longer acquisition time, dynamic mode offers superior reproducibility for neodymium. Neodymium measurement requires a double filament setup because the evaporation and ionisation processes occur at hugely different temperatures. The evaporation filament with the sample is kept relatively cool to promote stable and long lasting evaporation, while the much hotter empty ionisation filament allows efficient ionisation of Nd. Except for the double filament setup, the analytical procedure for Nd is very similar to strontium as described above.

The neodymium fractions were re-dissolved in 4 μ l HNO₃ of which half was loaded on pre-cleaned and outgassed double rhenium (annealed) filaments, again enabling a potential re-analysis. No TaCl₅ or any other activator is needed for Nd-analysis. Samples were heated slowly to an average temperature of about 1650 °C, before being properly focussed. The desired signal intensity was between 500 and 1000 mV ¹⁴⁴Nd.

Interference of ¹⁴⁴Sm on ¹⁴⁴Nd was monitored by measuring ¹⁴⁷Sm (¹⁴⁴Sm/¹⁴⁷Sm = 0.2049). A correction was applied, but samarium levels were normally very low (<< 1mV ¹⁴⁷Sm). A power law mass fractionation correction was used to counteract mass-dependant fractionation by normalising the measured ¹⁴⁶Nd/¹⁴⁴Nd ratio to the natural ratio of 0.721903. As a results of the dynamic routine, cup efficiency factors cancel out and the deterioration of the Faraday detectors is not an issue for the neodymium analyses. To check the reproducibility of the sample series, the in-house CIGO Nd-standard was measured at least once a day. Measured ratios for the CIGO standard are in good agreement with the long-term average at the VU *(see figure 3.5b)*. USGS reference materials BHVO-2 and BCR-2 are also within error of both the long-term average and literature values *(Weis et. al., 2006; see figure 3.5e,f)*. Just as for strontium, neodymium isotope composition for the whole bomb dissolved BCR-2 standard was within error the hotplate digested solution and in excellent agreement with recommended values.



Figure 3.5 – long-term replicate standard analyses with TIMS. Red symbols indicate measurements made during this sample series. Shaded areas denote 2 σ from average. **a)** NBS 987 strontium standard measured with the detector configuration used for this sample series. Note the trend away from the recommended value with time due to Faraday cup deterioration; **b)** in-house CIGO neodymium standard (recommended ¹⁴³Nd/¹⁴⁴Nd = 0.511342); **c)** and **d)** strontium-IC of BHVO-2 and BCR-2 USGS reference materials, normalised to NBS 987 = 0.710245. Dashed grey lines represent recommended values from Elburg et. al. (2005); **e)** and **f)** neodymium-IC of BHVO-2 and BCR-2 house from Weis et. al. (2006).

3.4 – Zircon in situ analysis

3.4.1 Zircon separation

Zircon was separated from the bulk sample using conventional mineral separation techniques at the Mineral Separation Laboratory at the VU Amsterdam *(see figure 3.6)*. After grinding the 6-8 kg rock samples in a jawcrusher, a ± 100 g representative aliquot was taken to provide for a whole rock powder. The remaining part of the sample was further reduced in grain size using a hardened steel disc mill. The sample was passed once through the disc mill set at 500 µm and twice at 250 µm. In between milling steps, the samples were sieved at 250 µm. The fraction coarser than 250 µm was passed through the disc mill again. After three milling steps, the coarse fraction (about 30% of the original sample) was put aside since the fraction <250 µm was estimated to yield >99% of the zircons. This fraction was used for subsequent zircon separation.

The $<250 \ \mu m$ fraction from the discmill was deslimed using a weak lye to eliminate any particles smaller than 30 μm , which are mostly clay particles. The desliming apparatus makes use of Stoke's law, which states that smaller particles will require a longer time to settle in a liquid under the influence of gravity than larger particles.

After drying, separation of zircon from the bulk of the sample was achieved primarily using heavy liquid separation. This technique makes use of density differences between minerals and a very dense liquid. Particles in that liquid will either float ($\rho_{particle} < \rho_{liquid}$) or sink ($\rho_{particle} > \rho_{liquid}$). At the VU Amsterdam, diiodomethane (CH₂I₂) is the heavy liquid of choice. Pure diiodomethane ($\rho = 3.34$ g/ml) can be mixed with dichlorobenzene to obtain any desired density. To speed up heavy liquid separation, it is performed in a liquid overflow centrifuge (LOC) to impose a much higher gravitational acceleration.

Since up to 90% of these granitoid samples is made up of quartz, plagioclase and alkali-feldspar, these minerals are first separated in a LOC-100 using diiodomethane with a density of 3.0 g/ml. Having a density around 2.5-2.6 g/ml, quartz and the feldspars will float while most other minerals (including zircon, $\rho \approx 4.6$ g/ml) are concentrated in the sink.



Figure 3.6 – flow chart for the zircon separation procedure
Due to the large amount of opaque ore minerals in the samples, the sink fraction was passed through an ore magnet first. Magnetic or easily magnetisable minerals will be drawn towards the magnet, while less magnetic minerals (including zircon) will not be affected. This process effectively removed most of the ore minerals (magnetite, ilmenite) and a major part of the biotite. The magnetic fraction was surprisingly large, almost 50% of the >3.0 g/ml fraction for sample MKS 36.

Subsequently, the non-magnetic fraction from the ore magnet was taken to the small centrifuge (LOC-50). Using diiodomethane with a density 3.3 g/ml, it was possible to take out biotite, hornblende and most of the pyroxene ($\rho < 3.3$ g/ml). The sink fraction represented a concentrate of heavy accessory minerals such as titanite, apatite and zircon.

Further separation using heavy liquids is impossible, but can be achieved using differences in magnetic susceptibilities amongst the accessory minerals. Compared to the other remaining minerals, zircon has by far the lowest magnetic susceptibility and will not be deflected even in a very strong magnetic field. The >3.3 g/ml sink fraction was first sieved into >180 μ m, 120-180 μ m, 90-120 μ m and <90 μ m fractions. All fractions but the <90 μ m fraction were processed individually in a Franz magnetic separator. By increasing the magnetic field strength after every pass, it was possible to obtain extremely enriched zircon fractions. Moreover, since metamict or cracked zircons have a slightly higher magnetic susceptibility, it was even possible to extract the most flawless zircons with the Franz magnet. The final, least-magnetic zircon fractions consisted of >99% zircon, with only very minor amounts of pyrite and an occasional apatite grain present.

Around 100 zircons were hand-picked from the least-magnetic fractions for each sample with the aid of a binocular microscope (group A). Care was taken to select inclusion and crack free, non-metamict zircons. Generally, the best grains resided in the 90-120 μ m sieve fractions. Besides the flawless zircons, an additional 5-10 metamict and anhedral zircons were picked from the more magnetic fractions (group B). Anhedral zircons, however, were extremely rare and usually turned out to be another mineral (probably apatite) altogether after cathode luminescence analysis. The selected zircons were mounted in clear epoxy resin and polished to expose their interiors in the Geological Technical Laboratory at the VU Amsterdam.

Cathode luminescence (CL) imaging was used to characterise zircon growth patterns, the presence of inherited cores and inclusions before laser-ablation analysis. Cathode luminescence is the emission of photons with a wavelength in the spectrum of visible light from the sample upon impingement by an electron beam in a weak vacuum *(Yacobi & Holt, 1990)*. Zones in a crystal with different trace element concentrations will respond differently to the electron beam and will therefore display different luminescence (colour, brightness etc.). CL-imaging was done using the cold cathode luminescence stage in the Optical Laboratory of the VU Amsterdam. An acceleration voltage of 18-19 kV resulted in an electron current of 500 mA and cathode luminescence of the zircons. High resolution photographs were taken of both the luminescent zircons as well as the same grains in transmitted light.

3.4.2 Laser-ablation ICP-MS analysis

Zircon U-Pb and trace element analysis was performed by laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) at the Faculty of Geosciences, Utrecht University. The laser-ablation setup consists of an infrared Lambda Physik ArF excimer laser with a wavelength of 193 nm coupled to a GeoLas optics system. Ablated material was carried to a Thermo Finnigan Element-2 ICP-MS by a steady flow of helium and argon gas. The laser was operated using a spot size of 30-40 µm and a repetition rate of 10 Hz, leading to an energy density of around 20 J/cm².

The Element-2 ICP-MS was tuned at the start of every measurement session to optimise signal intensity and keep mass bias to a minimum. Moreover, oxygen complex formation was taken into account by monitoring the ThO^+/Th^+ ratio. During every session, oxide interference and mass bias proved to be very low and not of significant influence to the results.

3.4.2.1 U-Pb analysis

Laser-ablation in situ U-Pb analysis of zircon requires very high quality analyses because an age resolution of better than 1% is desired. Simultaneous acquisition of lead and uranium isotopes generally results in the best results since it cancels out signal instability, but this is not possible with the single-collector Element-2. However, by keeping the magnetic field constant and only changing the electrical field, it is possible to rapidly scan across a range of masses. In this way, the Element-2 closely approximates simultaneous data acquisition. It was possible to analyse all masses from ²⁰⁰Hg to ²⁴⁸ThO by solely changing the electrical field at a constant magnetic field strength.

All four lead isotopes (²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb and ²⁰⁸Pb), ²³⁵U and ²³⁸U were measured. In addition, thorium was incorporated to provide Th-Pb ages. To allow a common-lead correction to be performed, ²⁰⁴Pb had to be accurately measured. Therefore, isobaric interference of mercury-204 (which is present in the plasma in small quantities) on ²⁰⁴Pb was corrected for by monitoring ²⁰⁰Hg and ²⁰²Hg, but mercury levels were normally very low. Oxide interference was monitored at mass 248 (²³²Th¹⁶O) but did not form a significant contribution either.

Around 50-60 individual grains were analysed per sample. To correct for mass and elemental fractionation *(see section 3.4.3)*, a standard-sample-standard bracketing procedure was adopted. The well-characterised Z91500 zircon standard was used as a calibration standard. This Proterozoic zircon megacryst standard has proven to be very homogeneous for U-Th-Pb isotopes *(Yuan et. al., 2004)* and is therefore an ideal candidate for an internal standard. Z91500 was measured 3-4 times before and after a sample series of 5-7 spots. Since spot size can be of influence on fractionation processes, spot size was fixed within a single series and a new series was started when changing the spot size. The result of this is that there are two measurement series per sample: one using a spot size of 30μ m and one with 40μ m. Every analysis was preceded by 30-45 seconds of baseline measurement with the laser off.

The use of Z91500 for calibration left us without a well-characterised zircon standard to use as an external standard. The lack of an external standard renders it impossible to determine the precision and reproducibility of the current laser-ablation setup and data normalisation software. This is a serious shortcoming in the zircon analyses and potentially inhibits publication of the zircon ages.

3.4.2.2 Trace element analysis

Zircon *in situ* trace element analysis was performed primarily to obtain titanium data for the Ti-in-zircon thermometer *(see section 6.3.3).* It was decided to include a selection of trace elements that could potentially be used to discriminate between groups of zircons with different U-Pb characteristics or morphology. Next to the rare earth elements, amongst others phosphorous, hafnium, thorium and uranium were incorporated in the trace element analysis.

Analyses were preferentially performed on grains that were also analysed for uranium-lead and were large enough to allow for multiple spots. Around 10 grains were selected per sample, a bit more for MKS 36. Zircons were measured in a standard-sample-standard bracketing procedure, with 3 calibration standards before and after a series of 5-7 samples followed by 2-3 external standards. Results were calibrated to NIST glass 612. A spot size of 30-40 µm was used. Data were acquired during 45 seconds preceded by 30 seconds blank measurement.

Offline time-integrated normalisation for instrumental drift and change in ablation rate was done using GLITTER software. Results for samples and external standard Z91500 were calibrated to NIST-612 glass standard using an assumed fixed concentration of 32.45 wt% (151,684 ppm) SiO₂ in zircon *(Anczkiewicz et. al., 2001)* measured on the interference-free isotope ²⁹Si.

The well characterised zircon Z91500 standard (*Wiedenbeck et. al., 2004*) was used as an external standard to monitor the accuracy and reproducibility of the laser-ablation analyses. Repeated analyses throughout the measurement session were reproducible to <10% (2 σ) for the heavy REE but yielded mean concentrations that were generally 20-30% too low compared to recommended values (*see figure 3.7*). Therefore it was decided to normalise trace element concentrations for all samples to the Z91500 zircon standard.

A major problem occurred in the analysis of titanium, the most important element in the trace element analysis. During the initial measurements session, titanium concentrations were measured on isotope ⁴⁷Ti. When processing the data offline however, it became evident that this isotope yielded erroneously high concentrations of titanium, in excess of 4000ppm. These concentrations indicate impossible zircon



Figure 3.7 – mean concentrations for 17 replicate analyses of the Z91500 zircon standard. Error bars are 2 σ . Recommended values are also plotted (Wiedenbeck et. al., 2004)

crystallisation temperatures exceeding 2000 °C *(Ferry and Watson, 2007).* After a scrupulous assessment to determine the source of error, I concluded that isobaric interference of doubly charged zirconium (⁹⁴Zr⁺⁺) most likely caused the problem. A quick check confirmed this suspicion: ⁴⁹Ti can not be affected by doubly charged zirconium. Multiple analyses of Z91500 standard using this isotope yielded reasonable Ti-concentrations.

Due to the destructive nature of laser-ablation, re-analysis using the proper titanium isotope (⁴⁹Ti) was not possible for every grain. During a second measurement session, using spot sizes of 20 and 30 μ m, it was possible to analyse 10-15 grains per sample for Ti-concentration only. Excluding other elements (except ²⁹Si that was required for calibration) allowed for longer acquisition times on ⁴⁹Ti, but still signal intensities were barely above the detection limit. Sample measurements were again normalised to NIST-612 glass assuming a SiO₂ content of 32.45 wt% in zircon and Z91500 was included as an external standard. Ti-concentrations in Z91500 are low (~6ppm) and measurements rarely exceeded the detection limit, rendering it unsuitable as an external standard. This implies that there is no reliable check on the quality of the Ti-concentration data.

3.4.3 U-Pb data reduction

Laser-ablation analysis is plagued by mass and elemental fractionation (Yuan et. al., 2004; Chang et. al., 2006), which can have multiple causes. To achieve high levels of precision, accurate correction for these fractionation processes is a prerequisite. Static fractionation is constant during ablation and predominantly caused by differences in ionisation efficiency and volatility of elements. Correction for static fractionation is relatively straightforward and is done by calibrating against a well-known standard using standard-sample-standard bracketing. A standard with a similar matrix is preferable since fractionation can be matrix dependant.

Time dependant elemental fractionation will also occur during ablation. Progressive ablation of the same spot alters the depth to width ratio of the pit leading to enhanced condensation on the pit wall. This favours the release of more volatile elements (e.g. lead). Due to this time-dependant fractionation, Pb/U-ratios will increase during a measurement. This type of fractionation is more difficult to correct for. Again calibration against a standard with a similar matrix is optimal. However, much more constraints are now put on the calibration standard. Any differences in matrix and hence response to the laser beam (i.e. ablation rate) will introduce non-linearity between sample and standard and introduce error. Since the fractionation is time dependant, care must be taken to compare data acquired in the same time interval during ablation.

Correction for the above mentioned interferences was performed using the open-source program Iolite *(Hellstrom et. al., 2008).* Prior to data reduction with Iolite, all analyses were checked for the contribution of common lead. Lead has one non-radiogenic isotope (204 Pb) that can be used as a monitor for the presence of common lead. This isotope however, does suffer from isobaric interference of 204 Hg introducing another correction factor. Fortunately, practically all analyses did not contain any significant common lead (final 206 Pb/ 204 Pb ratios >> 10,000). The 204 Pb signal intensity during data acquisition (i.e. during laser-ablation) was indistinguishable from the blank measurements prior to acquisition. It was concluded that correcting for common lead would only introduce error and therefore no common lead (206 Pb/ 204 Pb < 10,000); these were excluded from the final results altogether. Oxide interference was monitored by analysing mass 248, which represents 232 Th 16 O. Similar as for 204 Pb, signal intensities during data acquisition were identical to the blank levels. This means that the data files containing raw signal intensities in counts per second from the Element-2 ICP-MS could be imported into Iolite without any modification. One short note is that Iolite does not accept notations for an isotope such as 232 Th 16 O; the notation 248 Th should be used instead.

For time-dependant elemental fractionation correction, Iolite's data reduction scheme (DRS) for U-Pb geochronology was used *(Paton et. al., 2010).* This DRS requires a manual selection of baseline measurements, which are interpolated using a smoothed spline function. Next, calibration standards (Z91500) are selected to quantify the time-dependant elemental fractionation. The first few seconds of the measurement are excluded to eliminate the effect of surface contamination. The repeated standard measurements are plotted together in Pb/U plots versus time displaying the increase in Pb/U-ratios due to elemental fractionation. An exponential formula is fitted to the data. Iolite will offer a best-fit solution, but it is possible to manually adjust the fitting parameters to obtain a better fit. Subsequently, the derived exponential time-fractionation law is used to correct the sample measurements for fractionation. In general, time-dependant elemental fractionation proved to be quite limited for the laser-ablation setup used in this research project. Pb/U-ratios increased less than 10% with time in an almost linear fashion. Nevertheless, the exponential formulae were maintained. This implies that the fractionation correction is of limited influence to the final results and does not introduce a significant bias or error.

On the other hand, elemental fractionation was of influence in Pb/Th-ratios. The ²⁰⁸Pb/²³²Th versus time plot for the Z91500 standards was dissimilar to the Pb/U-ratios. Instead of a near-linear increase with time, the ²⁰⁸Pb/²³²Th vs. time curve had a parabolic shape. Obviously, an exponential formula will yield a poor fit to such a curve and hence correction for elemental fractionation between Pb and Th is far from optimal. It had been known already that the behaviour of thorium in the laser-ablation setup at Utrecht University was anomalous and difficult to correct for *(P. Mason, pers. comm.)*. The data acquired during this study are therefore in line with previous findings. For this reason, in this research project much less emphasis is placed on geochronological information derived from the thorium-lead decay system.

The Z91500 calibration standards were also used to correct for static mass fractionation as described above; this occurred automatically and simultaneously with the time-dependant fractionation corrections. The corrected and normalised data were subsequently exported to excel-files.

The final step in U-Pb data processing was to exclude certain analyses from the final data set and U-Pb age determinations. All analyses with too much common lead (final $^{206}Pb/^{204}Pb < 10,000$) were excluded. Additionally, the minimum data acquisition time was set at 20 seconds to avoid very short analyses. In this way, short analyses that are not necessarily representative are excluded. Finally, measurements that were considered to be aptypical during laser-ablation analysis were not incorporated into the results. These analyses were deemed unreliable due to various factors, e.g. increased signal instability, proximity of the laser-ablation pit to cracks, inclusions or grain boundaries etc.

3.5 – Feldspar thermometry

Ternary feldspars are feldspar grains that crystallised at high temperatures and, upon cooling, exsolved into separate plagioclase and alkali-feldspar lamellae. Exsolution of very sodium-rich (albitic) plagioclase lamellae from a alkali-feldspar host is the most common form. This perthitic exsolution frequently occurs in granitoid rocks and is caused by the solvus between orthoclase and albite. At higher temperatures, single feldspar grains can crystallise with a truly ternary composition, i.e. they include albite, anorthite and orthoclase components in more or less equal proportions. Exsolution can occur as plagioclase out of alkali-feldspar (perthite) or alkali-feldspar out of plagioclase (antiperthite). When it is impossible to tell which feldspar is the host and which one represents the lamellae, the ternary feldspar is named mesoperthite.

Since the solvus is temperature dependant, more ternary compositions can crystallise with increasing temperature. This allows the use of ternary feldspar compositions as a geothermometer. Calculation of a crystallisation temperature using this thermometer requires a single, ternary feldspar composition. Since the ternary feldspar will have exsolved upon cooling into plagioclase and alkalifeldspar lamellae, direct analysis of the ternary feldspar composition is impossible. To circumvent this problem, it is possible to obtain analyses of both the alkali-feldspar and plagioclase separately with the electron microprobe and use their relative proportions to calculate the original composition. The feldspar proportions can be estimated using image analysis of BSE images of the exsolved feldspar (*Štípská and Powell, 2005*).

The crystallisation temperature of the Bakhuis charnockites is estimated to be high based on mineralogical observations, but has never been established quantitatively. Since this temperature can provide an important piece of evidence for the charnockite-UHT relationship, ternary feldspar thermometry would form a major contribution to this thesis. However, time constraints prevented the inclusion of thermometry in the project. Fortunately, Suzette Timmerman, a highly motivated BSc-student with a particular interest in metamorphic petrology, wished to do a small research project within the Petrology group. Ternary feldspar thermometry of the Bakhuis samples proved to be an excellent opportunity for Suzette.

Due to the potential significance of the feldspar thermometry data, I have included the results in this thesis. I must stress the point however, that Suzette Timmerman is to be credited for all the work. She selected three charnockite samples and described the petrography in detail. Multiple ternary feldspar grains per sample were selected to be analysed with the electron microprobe. The analyses were carried out by Suzette. Due to several delays with the EMP however, she was pressed for time and did not have the opportunity to do all the data reduction before I had to finish this report. To be able to incorporate the results in my thesis, I have done the data reduction myself.

3.5.1 Electron microprobe analysis

Feldspar compositions were analysed using the Jeol JXA-8800M electron microprobe (EMP) at the VU Amsterdam. Selected thin sections were polished and coated with a thin veneer of carbon to enhance electric conduction. The EMP was operated at a acceleration voltage of 15 kV and a electron beam intensity of 25 nA. A defocused spot with a diameter of 10 µm was used due to the volatility and subsequent loss of sodium in a focussed beam. This however put severe restrictions on the grains to be analysed; exsolution of lamellae <20 µm was impossible to measure in spot mode. To overcome this problem, two different analytical techniques were used to analyse grains with fine exsolution. The first approach was a raster analysis, in which the electron beam is rapidly deflected across a selected area. The result is an average composition of the scanned area that represents the ternary feldspar composition. An advantage of this method is that it is very fast and that image analysis is not required; the data can therefore directly be used for thermometry. A similar but theoretically more precise technique is the map analysis. Again a rectangular area is selected that is divided into a grid of points. Every point is measured as an individual spot using a defocused beam of 15 μ m. If the points are placed sufficiently close together, the average of all the individual spots is the ternary feldspar composition. Since every point is measured individually, the results are generally more precise than in a raster analysis but the drawback is that the acquisition time is much longer.

For sample MKS 30, four grains with coarse exsolution were analysed by spot analysis. For every grain, measurements of the plagioclase host and alkali-feldspar lamellae were duplicated five times to obtain a representative analysis. Sample MKS 22 yielded two grains with coarse exsolution that allowed spot analysis similar to MKS 30. An additional three mesoperthitic grains characterised by very fine exsolution were included *(see figure 5.19)*. These were analysed using raster analysis and two of the grains were duplicated with a map analysis to check the accuracy of the raster technique. Unfortunately, sample MKS 20 proved not to contain any good quality ternary feldspars that were large enough to be analysed. Back-scatter electron (BSE) images were taken of every grain for image analysis.

Next to the regular feldspar constituents Si, Al, Ca, Na and K, analysed elements included strontium and barium *(see table 3.5).* It has been demonstrated that in the presence of Sr and Ba can cause overestimation of the ternary feldspar crystallisation temperature *(Essene et. al., 2005).* Therefore, these elements were included to monitor their influence on the modelled temperatures. Two in-house natural feldspar crystals (306-albite and 372-orthoclase) were incorporated as external standards to serve as an indication the precision of the EMP. Acquisition time for the major elements was 25 seconds on the peak and 12.5 seconds background; strontium and barium were measured for 36 seconds on peak and 18s background. All analyses were calibrated using a ZAF-method against natural and synthetic mineral standards.

Spectrometer	1	2	3	4
Crystal	TAP	TAP	PETJ	PETJ
	Si	Al	Ca	K
	Na			Ba
	Sr			

 Table
 3.5
 spectrometer
 setup
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3.5.2 Data reduction

The quality of the data was assessed by comparing the average compositions of the external standards to recommended values *(see table 3.6)*. The results were in overall agreement with the proposed composition of the standards, but it is evident that the quality of the data decreases drastically at low concentrations.

The ternary feldspar thermometer is weakly pressure dependant. A fixed pressure of 8.5 kbar is adopted, which is in line with suggestions by De Roever et. al. (2003) and De Groot (2007). A lower pressure will cause an overestimate of the temperature while a higher pressure has the opposite effect. A difference in pressure of 3 kbar however, will not influence the calculated temperatures more than 20 °C. Fuhrman and Lindsley (1988) calibrated a ternary feldspar thermometer that is considered to be most appropriate for (U)HT crustal rocks (Hokada, 2001; Štípská and Powell, 2005). Isotherms were calculated according to the Fuhrman and Lindsley (1988) thermometer using the freeware program SOLVCALC 2.0 (Wen and Nekvasil, 1994).

372 orthoclase	SiO ₂	Al ₂ O ₃	CaO	BaO	SrO	Na₂O	K₂O
1	62.56	19.50	0.12	1.06	0.37	1.45	14.95
2	62.82	19.36	0.12	0.98	0.35	1.46	14.91
3	62.08	19.84	0.11	1.05	0.36	1.45	15.12
4	62.67	19.46	0.10	1.01	0.34	1.42	14.99
5	61.91	19.84	0.10	1.04	0.35	1.49	15.27
recommended	64.18	18.38	0.08	0.94		1.39	14.47
average	62.41	19.60	0.11	1.03	0.35	1.45	15.05
%RSD (2σ)	1.25	2.29	17.45	6.44	5.23	3.63	1.93
deviation	-2.76	6.64	40.80	9.35		4.54	3.98
306 albite	SiO ₂	AI_2O_3	CaO	BaO	SrO	Na ₂ O	K₂O
1	66.75	20.59	0.07	0.00	0.23	12.22	0.13
2	67.00	20.59	0.09	0.00	0.23	11.95	0.14
3	67.58	20.14	0.07	0.00	0.22	11.86	0.13
4	67.35	20.24	0.10	0.00	0.23	11.94	0.15
5	66.78	20.60	0.07	0.02	0.23	12.17	0.13
recommended	68.60	19.45	0.05			11.60	0.14
average	67.09	20.43	0.08	0.00	0.23	12.03	0.13
%RSD (2σ)	1.08	2.20	35.81	398.62	5.30	2.65	13.09
deviation	-2.20	5.05	60.89			3.70	-4.29

Table 3.6 – average analyses of two natural, in-house feldspar standards included as unknowns in the sample series. Relative alkali-feldspar and plagioclase proportions were determined by image analysis of the BSE images using the freeware program ImageJ (*Rasband, 1997*). Images were imported into the program and cropped to display only the ternary feldspar part. Subsequently, the image was made binary so that plagioclase was black and alkali-feldspar white. Pixel counting of a selected area was used to determine the percentage of black pixels, i.e. the percentage of plagioclase. The pixel counting was replicated 5-8 times on slightly different areas and averaged to ascertain a representative estimate of feldspar proportions. The standard deviation (2σ) of the multiple pixel analyses was usually better than 5%.

For every grain measured with spot analysis, the five individual alkali-feldspar and plagioclase analyses were averaged to ensure a representative measurement. Variation between the different spots was very small and only one obvious erroneous outlier was excluded from the results. In conjunction with the relative feldspar proportions obtained with image analysis, these average compositions were used to calculate the ternary feldspar composition. Using isotherms plotted with SOLVCALC, the calculated and the directly measured (map and raster analyses) ternary feldspar compositions were solved graphically to yield temperatures.



Figure 3.8 – *Ternary feldspar isotherms calculated with solvCALC 2.0 using the model of Fuhrman and Lindsley* (1988) *at a pressure of 8.5 kbar.*

Chapter 4 – Field relationships and petrography

4.1 – Igneous charnockites and xenoliths

Magmatic charnockites were sampled in the southwestern part of the Bakhuis granulite belt. The Kabalebo airstrip served as a hub from which multiple expeditions were organised along the rivers and into the jungle *(see figure 4.2a).* While outcrops are rare in the jungle due to the intense tropical weathering, they are copious in the riverbeds of major streams. These outcrops are submerged for most part of the year and are only exposed during the dry seasons (February-March and August-December). The low water level however, is disadvantageous for navigation by boat. It was for instance impossible to continue past Krong Soela in the south. Despite the superior access to outcrops, a major disadvantage of sampling along the Kabalebo river is its proximity to the western shearzone that bounds the Bakhuis horst. Many samples are heavily deformed, regularly making it hard to interpret petrographic textures. Outcrops of sheared biotite-granite augengneiss are also found along the river. For this reason, emphasis was placed on sampling southeastwards from the Kabalebo river into the interior of the horst. Rocks less affected by the mylonitisation are presumed to occur along the Kilo Drie and Zand creeks for instance.

In this section, the field relationships and petrography of the igneous charnockite suite will be discussed. The samples are grouped per sampling location and divided into five groups: Kilo Drie creek, Misty Mountain, Krong Soela and the stretch of river directly to the northeast, Zand Creek and Moi-Moi. All sampling locations are depicted in figure 4.1, a map of the southwestern part of the Bakhuis horst. First, a general overview of the petrography of the charnockites will be provided, followed by detailed descriptions of the variation in and between the sample groups and field-relationships.

4.1.1 Charnockite petrography

The typical mineral assemblage for the Bakhuis charnockites is: quartz, alkali-felspar, plagioclase, orthopyroxene, clinopyroxene and biotite *(see figure 4.3c,d)*. Hornblende is frequently present as well while zircon and apatite are very common accessory phases. A notable feature of the charnockites is the abundance of opaque ore minerals. These are partly of secondary origin as they can be seen to fill extensional veins related to the mylonitisation, but they are predominantly primary.

Orthopyroxene can be recognised by its high relief combined with subtle pink-mint green pleochroism and can be distinguished from clinopyroxene by its higher birefringence and straight extinction. For small or anhedral grains however, the distinction between opx and cpx is often troublesome since cleavage is poorly developed. Biotite shows strong colourless to reddish-brown pleochroism and its planar cleavage is unique amongst the charnockite mineral assemblage. Hornblende is easily distinguished based on the typical cleavage and pleochroism. The colour of hornblende is variable between olive-green and dark brown and in rare cases blue-green hornblende can be seen (see figure 4.8a,b). Quartz occurs sporadically as larger crystals, but in the majority of the samples it has experienced intense dynamic recrystallisation and grain-size reduction. The few large grains are not devoid of deformation either since they invariably display undulose extinction. Plagioclase is characterised by albite twinning while Karlsbad twins are frequent in both feldspars. In addition to the twinning, alkali-feldspar can be distinguished by its lower birefringence compared to plagioclase and dusty appearance. Feldspar exsolution occurs extensively in the charnockites and perthite, antiperthite and mesoperthite are all present. For the anti- and mesoperthite, exsolution occurs as blocky patches or in a vermicular form; mesoperthite can also have the shape of micrometer-sized lamellae: microperthite (see figure 4.5a). Myrmekitic quartz-plagioclase intergrowths are not uncommon. Accessory phases apatite and zircon are abundant in the charnockites. Apatite forms euhedral, stubby to elongate crystals that are clearly recognisable by their high relief and low birefringence. Zircon appears to be more subhedral and has a dirty appearance. Similar to apatite, it stands out by its high relief but it has a much higher birefringence resulting in bright second order interference colours.

The charnockites suffered greatly from mylonitisation as a result of the proximity to the shearzone that bounds the Bakhuis horst. Despite the pronounced recrystallisation, most samples still retain a clearly magmatic texture. The samples are characterised by a porphyritic texture with large (up to 1 cm),

euhedral plagioclase grains in a medium-grained matrix. This texture is hard to discern in a hand specimen, but obvious under a polarisation microscope. Plagioclases is often strongly zoned, occasionally in combination with antiperthitic exsolution in the rims. Moreover, Karlsbad twinning is common in the charnockites, a feature typical of igneous rocks but normally rare in metamorphic feldspars. Alkalifeldspar, ortho- and clinopyroxene can also occur as euhedral grains and more rarely hornblende has a euhedral habit. In highly deformed samples, quartz is completely recrystallised and the mafic minerals have clotted together in schlieren-like bands *(see figure 4.3b,e,f)*. In the bands, pyroxene crystals appear to be broken into smaller bits that are surrounded by fine-grained biotite. Moreover, feldspar crystal can display signs of deformation as well in the form of incipient sigma-klasts. Hornblende occurs both as a primary phase and as secondary replacement of pyroxene.



Figure 4.1 – sketch map of the research area at Kabalebo. The location of the Bakhuis Mountains and the Blanche Marie Falls are indicated in the inset. Coordinates are standard UTM-grid (WGS 84).





Figure 4.2 - field relationships; a) typical outcrop in the Bakhuis Mountains. This locality is situated along the Zand Creek; b) intrusive contact of the light coloured charnockites and a darker unit at the top of the large rapid in the Kilo Drie creek. Rock hammer (40 cm) for scale; c) granulitic xenolith in the charnockites at Krong Soela. Note the conspicuous banding in the xenolith and the resorption around the lower contact giving the xenolith a restitic appearance. Rock hammer for scale; d) large granulitic xenolith in the charnockites at Krong Soela. Note the charnockitic veins throughout the block. Rock hammer for scale; e) contact between the charnockite and metagabbro at Moi-Moi. The charnockitic vein is clearly intrusive in the gabbro as demonstrated by the small tapered vein in the lower left corner. Rock hammer for scale.

4.1.2 Misty Mountain

The Misty Mountain series was sampled along a well maintained trail through primary forest starting opposite to the Kabalebo airstrip. The first 2-3 kilometres, outcrops are very scarce. Sample MKS 17 is taken from an outcrop on a small hill along the path northwest of Misty Mountain. At the locality of MKS 18, the trail splits; one path continues to the summit of Misty Mountain while the other path veers to the east and ends up at the waterfall on the northeastern side of the mountain. The northwestern slope of Misty Mountain along the trail was sampled systematically. Samples for zircon geochronology and geochemistry were taken at the foot and summit (MKS 19 and 22 respectively) while three samples were collected at a quarter, halfway and three quarters up the slope (MKS 23, 20 and 21 respectively) for geochemistry. Despite the relative abundance of outcrops, they are isolated and range in size up to 5 metres at maximum. This makes defining field relationships impossible, especially since the surface of the rocks is severely weathered.



Figure 4.3 – textures of the magmatic charnockites; **a**) transmitted light, example of an undeformed charnockite (MKS 22, Misty Mt.); **b**) transmitted light, example of a highly sheared charnockite (MKS 18, Misty Mt.) in which the mafic minerals have clotted together in schlieren-like bands; **c**) PPL, aggregate of hornblende (light coloured grains on the left), orthopyroxene (heavily cracked mineral top right) and clinopyroxene (between the opx and hbl with apparent planar cleavage) in sample MKS 22 (Misty Mt.). Note the abundant opaque minerals; **d**) XPL, the same as c). The cpx grain stands out by its brighter interference colours; **e**) PPL, schlieren-like band of two pyroxenes, fine-grained biotite and minor hornblende in sample MKS 18 (Misty Mt.); **f**) XPL, the same as e)

Samples on the slope and top of the mountain are relatively undeformed. Quartz does exhibit undulose extinction, but has not suffered the degree of recrystallisation witnessed by most other samples. It appears that this lack of intense deformation is related to the existence of Misty Mountain and the abundance of outcrops in its slopes; the mountain is by far the most pronounced topographical feature in this part of the Bakhuis horst. Apparently, the low degree of deformation has made the mountain more resistant against weathering. An advantageous consequence of the limited recrystallisation is that original textures have been better preserved. Samples from Misty Mountain display multiple petrographic indications of

high crystallisation temperatures. Feldspar exsolution for instance is a common feature and mesoperthite occurs in samples MKS 19 to 23 and MKS 30 (see figure 4.5). Exsolution occurs predominantly as blocky patches or in a vermicular form, but fine microperthite is also present. See sections 3.5 and 5.4 for a more detailed description of feldspar thermometry. Samples MKS 21 and 22 taken at and near the summit of the mountain contain large crystals of bright blue quartz. The blue colour is caused by the presence of fine rutile needles or colloidal TiO₂ in the quartz, which is typical for high temperature rocks (Deer et. al., 1992, Wark and Watson, 2006). A third indication for high crystallisation temperatures is formed by the occurrence of inverted pigeonite in one of the Misty Mountain samples. Pigeonite is a high-temperature pyroxene with a composition intermediate between hyperstene and augite. A single pigeonite grain crystallised at a high temperature will, upon cooling of the rock, exsolve or invert into separate ortho- and clinopyroxene parts. Inversion occurs at around 950 °C for ferroan pigeonites and up to 1100 °C for very magnesium-rich crystals (Deer et. al., 1992). Sample MKS 22 contains multiple excellent examples of inverted pigeonite with thin clinopyroxene lamellae in an orthopyroxene host (see figure 4.4). Besides these characteristic features, the petrography of the Misty Mountain suite is not different from the general description provided in section 4.1.1. Hornblende is a common phase and forms euhedral crystals with olive green to brown-green pleochroic colours.

Sample MKS 17 is strikingly different to the general charnockite petrography as it does not contain clinonor orthopyroxene. It is however, similar to sample MKS 35 from the Zand Creek suite *(see section 4.1.4)*. Hornblende does occur, but is characterised by blue-green pleochroic colours *(see figure 4.8a,b)* and forms isolated euhedral crystals. Moreover, this sample contains abundant subhedral titanite crystals, a phase not seen in any of the other samples except for MKS 35. Titanite is characterised by a high relief, weak orange- to reddish-brown pleochroism and very high birefringence *(see figure 4.8c,d)*. Biotite is present as sub- to euhedral crystals, as well as both feldspars and deformed quartz. Contrary to the other Misty Mountain samples, there are no high temperature indicators present; exsolution is non-existent in the feldspars.



Figure 4.4 – inverted pigeonite in sample MKS 22 (Misty Mt.). The host mineral is orthopyroxene, which contains lamellae of clinopyroxene (purple-blue in XPL) that have exsolved upon cooling. The presence of inverted pigeonite is indicative of crystallisation at temperatures in excess of 950 °C (Deer et. al., 1992); **a**) and **c**) PPL; **b**) and **d**) XPL.



Figure 4.5 – examples of anti- to mesoperthitic feldspar. The lighter grey colours represents plagioclase while alkali-feldspar is darker grey; **a**) XPL, vermicular mesoperthite and microperthite in sample MKS 22 (Misty Mt.); **b**) XPL, exsolution as blocky patches in sample MKS 30 (Misty Mt. waterfall).

See also figure 5.1 for back-scatter electron images of feldspar exsolution and front cover of this thesis.

The discussion so far has focussed on a NW-SE transect from the Kabalebo river to the summit of Misty Mountain. A large outcrop at a waterfall on the northern slope, approximately 1 kilometre from the top of the mountain, was also investigated (see figure 4.1 and 4.6a). Here, charnockite (sample MKS 30) was found that was highly similar in petrography to the other Misty Mountain samples. No blue quartz was present, but mesoperthite was abundant and occurred predominantly as blocky patches (see figure 4.5b). The importance of the outcrop at the waterfall however, lies in the presence of many angular mafic xenoliths ranging in size from 5 to 50 cm. Unfortunately, exposure was not sufficient to study field relationships in detail and it is not possible to state the nature of the contact between the charnockite and mafic xenoliths without ambiguity. Samples of five xenoliths have been taken for petrographic examination: samples MKS 31a-d and MKS 32. The xenoliths have an igneous porphyritic texture with large (up to 1cm), sub- to euhedral, long prismatic plagioclase phenocrysts in a fine-grained groundmass of clinopyroxene, euhedral plagioclase and brown hornblende (see figure 4.7c,f,g). The plagioclase phenocrysts often display Karlsbad twinning in combination with albite twins. Grain size is slightly variable between the xenoliths, but otherwise they are identical. The lath-shaped, euhedral plagioclase crystals in a fine-grained groundmass are reminiscent of an ophitic texture; the difference is the ubiquity of hornblende that is present in equal proportions or slightly more abundant than clinopyroxene. In addition to the introduction of hornblende, later-stage recrystallisation is evident from resorption along plagioclase grain boundaries. Although there is little doubt that these xenoliths represent igneous rocks, they have obviously suffered from a metamorphic event and hence are classified as metadolerites.

Dolerite intrusions with an age around 1.8 Ga (Avanavero dolerite) are known to occur in western Suriname, but these do not show the recrystallisation of the groundmass pyroxenes. Moreover, the texture of the metadolerite is at odds with the hornblende-free and much coarser Avanavero dolerite *(E. de Roever, pers. comm.).* The possibility that these xenoliths belong to the granulite suite is precluded by the igneous texture, but they could represent a symmetamorphic intrusion.

4.1.3 Krong Soela

The Krong Soela suite of samples comprises the outcrops at a large rapid named Krong Soela ("soela" means "rapid" in the local language) and two outcrops along the Kabalebo river a few kilometres north of the soela. The rapid consists of a northern and a southern part separated by ~ 100 metres of deeper river. Both parts are wide enough to cover the entire river and, due to the low water level, it was impossible to venture beyond the northern part by boat *(see figure 4.6b)*. Instead we had to wade through the river to get to the larger southern part of the rapid. This part offered almost continuous exposure for over 200 metres, which allowed detailed inspection of field relationships. Similar to the outcrop at the Misty Mountain waterfall, the charnockite at Krong Soela contained abundant mafic xenoliths up to 1.5 metres in size. Closer inspection of the xenoliths revealed that they were completely

different from the metadolerite xenoliths encountered at the waterfall. Compositional banding at the centimetre-scale and foliation were widely present in the xenoliths and easily visible in the field (see figure 4.2c). The shape of the xenoliths was often blocky and the contacts with the charnockite were irregular. Veins of the charnockite were seen to intrude into the xenoliths (see figure 4.2d) and resorption appeared to occur on the xenolith-charnockite interface (see figure 4.2c). These observations preclude a comagmatic origin for the xenoliths: they do not resemble smooth, rounded mafic enclaves. Petrographic analysis of six hand specimens (samples MKS 24a-f) confirmed this conclusion. The texture was highly different from the Misty Mountain waterfall xenoliths. All xenoliths have an equigranular habit, exhibit a weak foliation and consist predominantly of olivegreen to brown hornblende and plagioclase with ubiquitous albite twinning (see figure 4.7a,b,c,d). As is evident from figure 4.2a and b, grain size varies between fine and intermediate. Pyroxene is present in variable amounts from a few grains to equal proportions to hornblende. The occurrence of orthopyroxene is indicative of granulite facies metamorphism and hence these samples are named mafic granulites. As will be discussed later, the Krong Soela xenoliths are similar in petrography to the mafic hornblende-pyroxene granulites found in the Blanche Marie area (see section 4.2). Field relationships suggest that the xenoliths are blocks of granulitic country rock incorporated in the magma. Another possibility is that they are restitic xenoliths, i.e. bits of the protolith that have not melted completely, which finds support in the following reasoning. All xenoliths encountered at Krong Soela are mafic granulites while no intermediate or felsic counterparts are found. This is incompatible with the general composition of the Bakhuis granulite suite that consists of approximately 30-35% mafic granulites. It is therefore possible that the felsic and intermediate granulites have melted to form the charnockitic magma, while a small amount of mafic granulite was residual and incorporated in the magma as restites. The resorption seen around some of the xenoliths is also suggestive of a restitic origin, but is not incompatible with country rock assimilation either.



Figure 4.6 – photographs of outcrops in the Bakhuis Mountains; **a)** the waterfall on the northern slope of Misty Mountain; **b)** Krong Soela, a large rapid in the Kabalebo river. In the photo are my supervisor E. de Roever and our local guide Jogi; **c)** the waterfall at Moi-Moi. The lithology from where the photo is taken is charnockite, the waterfall itself consists of gabbro.



Figure 4.7 – xenoliths found at Misty Mountain waterfall and Krong Soela; **a**) transmitted light, texture of a coarse hbl-px-granulite xenolith from Krong Soela (sample MKS 24c); **b**) transmitted light, texture of a fine hbl-px-granulite xenolith from Krong Soela (sample MKS 24d). Note the weakly developed foliation and lack of lath-shaped plagioclase phenocrysts; **c**) transmitted light, texture of a dolerite xenolith from Misty Mt. waterfall (sample MKS 31a). Note the presence of lath-shaped plagioclase phenocrysts; **d**) PPL, equigranular texture of fine-grained hbl-px-granulite xenolith MKS 24d with plagioclase olive-green hornblende and clinopyroxene (lower right); **e**) XPL, the same as d); **f**) PPL, porphyritic texture of dolerite xenolith MKS 31a. Note the lath-shaped plagioclase phenocrysts that exhibit Karlsbad twinning and minor resorption in a groundmass of clinopyroxene, hornblende and plagioclase; **g**) XPL, the same as f).

Whether the xenoliths are blocks of country rock or restites remains ambiguous, but nevertheless several conclusions can be drawn based on the field relationships at Krong Soela. The mafic xenoliths are similar to the mafic hornblende-pyroxene granulites found at Blanche Marie, which are a fundamental constituent of the metamorphic suite. This provides a relative age relationship indicating that the charnockite magmatism postdates metamorphism. Country rock assimilation implies that the charnockites are intrusive into the metamorphic suite while a restitic origin designates that they are partial melts of the granulites.

Two charnockite samples were taken from the southern part of Krong Soela. Sample MKS 25 was taken at the eastern shoreline above the mean water level in the proximity of abundant xenoliths. This sample contains little quartz and hornblende and resembles the Kilo Drie samples *(see section 4.1.6)*. Biotite, ortho- and clinopyroxene form euhedral crystals and show no signs of strong deformation. Plagioclase occurs as large (up to 0.8 cm), strongly zoned, euhedral grains that are weakly aligned. Antiperthitic exsolution occurs in plagioclase rims, indicative of zoning from a more calcic core to a more sodic rim. The alignment of the plagioclase phenocrysts suggests a cumulate-texture. MKS 26 was sampled at the centre of the rapid and was selected for zircon geochronology. Its petrography is in good agreement with the general charnockite description in section 4.1.1, but the amount of hornblende is below average. A foliation is present as witnessed by lineation of pyroxene grains.

The northern part of Krong Soela is much smaller than the southern part and measures approximately 5 by 10 meters. Inspection in the field indicated that the xenoliths in the northern part are similar to those in the southern part and they were therefore not sampled. A charnockite sample was taken here: MKS 27. This sample is in line with the general description. Compared to samples MKS 25 and 26, deformation is more intense and mafic minerals plus opaques are grouped in schlieren-like bands *(see figure 4.3b,e,f)*. Anti- and perthitic exsolution as blocky patches ranges up to 25% exsolution; not enough to categorise these feldspars as mesoperthites.

Two additional charnockite samples were taken from outcrops along the Kabalebo river \sim 800m (MKS 28) and \sim 3.5km (MKS 29) north of Krong Soela *(see figure 4.1)*. The proximity to the boundary shearzone is reflected in the highly deformed character of MKS 28. Pyroxene grains are broken into smaller pieces and concentrated in schlieren-like bands together with hornblende and fine-grained biotite. Quartz is completely recrystallised and feldspar exsolution is non-existent. Sample MKS 29 is much less deformed and feldspar exsolution approaches mesoperthite. Both samples are similar to the Krong Soela samples as they contain little hornblende: biotite, opaque minerals, ortho- and clinopyroxene are all more abundant than hornblende.

4.1.4 Zand Creek

The Zand Creek is a major tributary of the Kabalebo river and extends southwards into the central part of the Bakhuis horst. Hence, the creek potentially allows access to less deformed charnockites. Due to the low water level and abundance of small rapids in the Zand Creek, it was impossible to enter by boat. Therefore, we used a small canoe to travel upstream for about 7 kilometres *(see figure 4.2a).* Here we reached another large rapid that was difficult to pass. Moreover, time constraints made us decide not to venture further than this rapid. Four samples were taken along the Zand Creek from isolated outcrops. Xenoliths or mafic bands were not encountered.

MKS 33 is the northernmost sample taken relatively close to Misty Mountain *(see figure 4.1).* Its petrography is also reminiscent of the Misty Mountain series as it is characterised by an almost complete lack of foliation. Quartz forms large undulose crystals and the mafic minerals are undeformed. Notable of this sample is the common occurrence of myrmekitic quartz-plagioclase intergrowths. Feldspar exsolution as blocky patches is at maximum 20% and the amount of apatite is above average. Brown hornblende on the other hand is not as common as in the Misty Mountain samples and is subordinate to both pyroxene and biotite.

After a long stretch of river without decent outcrops, MKS 34 was sampled approximately 4 kilometres south of MKS 33. This sample has suffered significant mylonitisation: quartz is recrystallised and the mafic minerals are clotted together in bands. Opaque minerals are more abundant than biotite, ortho- and clinopyroxene. Due to the occurrence of very fine-grained biotite but complete absence of hornblende, MKS 34 resembles the Kilo Drie samples and MKS 25 from Krong Soela.



Figure 4.8 – textures of the anomalous samples MKS 17 (Misty Mt.) and 35 (Zand Creek); **a)** PPL, euhedral hornblende phenocrysts in MKS 17; **b)** PPL, same as a) but with the polariser rotated 90°. Note the pronounced blue-green pleochroism of the hornblende. Colourless to reddish-brown pleochroism of biotite is also well visible in the top-right corner; **c)** PPL, subhedral titanite crystals in sample MKS 17; **d)** XPL, the same as c). Note the high order interference colours of titanite.

One kilometre south from MKS 34, an anomalous sample was encountered. MKS 35 is similar to MKS 17 from the Misty Mountain series in that it does not contain clino- nor orthopyroxene. Hornblende is present as sub- to euhedral isolated crystals and finer-grained, anhedral aggregates. It is characterised by blue-green pleochroism as opposed to the regular olive-green to brown pleochroism *(see figure 4.8a,b)*. Analogous to sample MKS 17, subhedral titanite grains are also present *(see figure 4.8c,d)*. Sample MKS 35 is much finer grained and contains less opaque minerals than the average charnockite sample. Another distinguishing feature is the predominant occurrence of perthitic exsolution as opposed to antiperthite for the other charnockites. MKS 35 has a weak foliation and quartz is partly recrystallised. Apatite and zircon inclusions are common in the feldspars.

The southernmost outcrop examined during the field campaign lies about 200 meters north of the large rapid mentioned above. Here, a dark-coloured, non-foliated charnockite was sampled for geochemistry and zircon geochronology: MKS 36. In line with sample MKS 34, hornblende is absent. Clinopyroxene, orthopyroxene, biotite and opaque minerals are usually clotted together in clusters but not in schlieren-like bands. The most conspicuous feature of sample MKS 36 are the large (1cm max.), euhedral plagioclase crystals. Many of these large plagioclase crystals are strongly zoned and characterised by antiperthitic exsolution in the rims. This texture resembles sample MKS 25 from Krong Soela, but lacks the clear plagioclase alignment. Zircon is especially abundant in this sample and appears to be enriched.

4.1.5 Moi-Moi

Moi-Moi is a waterfall located more or less halfway between the Kilo Drie creek and the airstrip, about 500m into the jungle from the Kabalebo river *(see figure 4.6c)*. A well maintained trail leads from the river to the waterfall where the path bends to the SW and continues to the start of the Misty Mountain trail. The lower part of the waterfall consists of dark-coloured, heavily deformed charnockite: sample MKS 38. This sample was selected for zircon geochronology. It is characterised by the presence of brown hornblende that appears to be replacing orthopyroxene. Finer-grained brown-green hornblende and biotite are also present but subordinate to the brown hornblende and pyroxenes. Feldspar is generally anhedral but does display Karlsbad twinning; quartz is scarce.

The locality at Moi-Moi however, deserves attention by the lithology exposed at the upper part of the waterfall. Here, a coarse grained metagabbro is the dominant lithology. Sample MKS 37 was taken from the gabbro for petrography and geochemical analysis. The metagabbro contains pyroxene, plagioclase and two populations of hornblende. It has an ophitic texture similar to the metadolerite xenoliths *(see section 4.1.2 and figure 4.7c,f,g)* with euhedral, lath-shaped calcic plagioclase crystals in an intermediate-grained groundmass consisting of clinopyroxene and hornblende. The groundmass hornblende displays greyish-blue to green pleochroism. This resembles samples MKS 17 and 35 (see figure 4.8a,b), but the blue pleochroism is less pronounced. Plagioclase regularly exhibits Karlsbad and albite twinning. The plagioclase crystals are overgrown by the second population of hornblende in a poikilitic texture *(see figure 4.9)*. These euhedral hornblende oikocrysts are bronze-coloured and range in size up to 1 cm. It appears that the bronze-coloured hornblende oikocrysts are a magmatic phase while subsequent recrystallisation of groundmass pyroxene formed the blue-green hornblende. The texture of the gabbro suggests that it is a coarser-grained equivalent of the metadolerites that has experienced subsequent recrystallisation.

The field relationships at Moi-Moi indicate that the charnockite is intrusive in the metagabbro. Sharp, centimetre-sized veins of light-coloured charnockite intrude the metagabbro *(see figure 4.2e)*. The metagabbro does not display chilled margins and is coarse grained near the contact with the charnockites. These observations are at odds with a comagmatic origin of the metagabbro and charnockites. Rather, the charnockite is intrusive in the metagabbro and therefore postdates gabbro emplacement. Geochemical data are required to illuminate this matter.



Figure 4.9 – sample MKS 37: the metagabbro from Moi-Moi; transmitted liaht, the a) poikilitic texture with brown hornblende oikocrysts. Note that the finer grained hornblende has a less brown colour; b) XPL, hornblende oikocryst enclosing multiple euhedral, lath-shaped plagioclase crystals.

4.1.6 Kilo Drie creek

The small Kilo Drie creek is situated in the northern part of the research area and leads southeastwards from the Kabalebo river into the interior of the Bakhuis mountains. Since the stream was far too small to negotiate by boat, we followed a small, overgrown trail along the creek upstream for about three kilometres. Here we encountered a large, well exposed rapid. The trail appeared to end here and, after sampling this location, we decided not to venture further into the jungle. Samples MKS 14 and 16 were taken at the lower edge of the rapid along the trail in the bush, while MKS 15 was sampled at the top of the rapid. Field relations were difficult to interpret in the small forest outcrops, but the exposure at the top of the rapid offered more clarity. Here, a light-coloured magmatic lithology is seen to be intrusive in a darker unit. The dark lithology forms elongate lenses that resemble boudins and, together with the

light-coloured lithology, shows obvious signs of strong deformation. Centimeter-sized veins of the lightcoloured lithology intrude the dark lenses *(see figure 4.2b)*. This provides sound evidence for an intrusive contact rather than boudinage of previously existing compositional banding. The light-coloured rock is a pyroxene-bearing granitoid: igneous charnockite. Sample MKS 15 was taken from one of these lightcoloured bands. The darker lithology was regarded in the field to be part of the metamorphic granulites: fine grained but no clear foliation. However, petrographical examination of two previously obtained pieces of the dark lithology, revealed that one piece has a relic ophitic texture resembling the metadolerites. For the second piece, intense mylonitisation has obliterated the original texture. It appears to be a pyroxene-rich medium grained granulite. These two pieces suggest that the dark lithology represents a recrystallised dolerite-gabbroic intrusion. Careful re-evaluation in the field and better sampling of the dark-coloured units is required to elucidate the field relationships at the Kilo Drie rapid.

All three samples from the Kilo Drie stream are highly similar in petrography. They all contain orthopyroxene, approximately half of which occurs as isolated subhedral grains. The other half is finer grained and situated in the schlieren-like bands *(see figure 4.3b,e,f)*, closely associated with very finegrained biotite and opaque minerals. Biotite is also present as sub- to euhedral isolated grains. Plagioclase and alkali-feldspar are coarse grained and sub- euhedral. They occur in more or less equal proportions. Quartz is present in very fine grained recrystallised bands. It is rare in MKS 14 but occurs more frequently in samples MKS 15 and 16. The most conspicuous feature of the Kilo Drie series however, is the total absence of hornblende. This is in sharp contrast with the other sampling localities where hornblende is a common phase. Due to the clear field relationships at the top of the rapid, sample MKS 15 of the Kilo Drie series was selected for trace element and radiogenic isotope analysis.

4.2 – Metamorphic suite

The metamorphic granulites of the Bakhuis mountains were sampled for comparison to the magmatic charnockites. It was endeavoured to obtain the most representative selection of samples of the metamorphic suite, sampling all occurring lithologies. A detailed petrographic study of the granulites lies outside the scope of this project and therefore the petrography will only be discussed briefly. Samples of the granulites were predominant taken from outcrops in area around the Blanche Marie Falls (see figure 4.10), a large waterfall in the Nickerie river about 75 km to the northeast from Kabalebo (see figure 4.1). One sample was taken along the Kabalebo river north of the Kilo Drie creek.



Figure 4.10 – the Blanche Marie Falls in the Nickerie river

4.2.1 Blanche Marie and drill core samples

Due to heavy rainfall after leaving Kabalebo, the water level in the rivers had risen dramatically when we arrived at Blanche Marie. As is evident from figure 4.10, the waterfall offers excellent exposure of the metamorphic suite and its field relations *(see figures 2.1d and 2.3b)*. Unfortunately however, it proved to be impossible to reach the upper part of the waterfall because of the torrential river. All samples were therefore taken from small outcrops along the western bank of the Nickerie river that was accessible by a trail. This restricted the choice in sampling and the Blanche Marie samples are not the best examples of the metamorphic suite. My supervisor E. de Roever kindly provided a drill core from his own collection to improve the selection of metamorphic samples. Drill core LA 156 was taken in the centre of the Bakhuis belt *(see figure 2.4)* and contains pristine granulites. Figure 4.11 provides an overview of the textures of the metamorphic samples. The samples are grouped into two categories: mafic and intermediate granulites. Sample MKS 56 did not fit into the categories and is treated separately.

4.2.1.1 mafic granulites

The mafic granulites comprise samples MKS 42, 43, 44, 51, 52 and 53. They are similar in petrography to the hbl-px-granulite xenoliths from Krong Soela *(see figure 4.7a,b,d,e)*. Characteristic for these samples is the equigranular mineral assemblage of plagioclase, hornblende, clino- and orthopyroxene. Grain size is variable *(see figure 4.11c,d)* and also the amount and relative proportions of ortho- and clinopyroxene vary widely. All samples contain orthopyroxene and can therefore be classified as granulite facies. In sample MKS 51, pyroxene can be seen to replace hornblende, indicative of prograde metamorphism *(see figure 4.11f)*. Plagioclase often displays albite twinning and hornblende varies in colour from brown-green to brown.



Figure 4.11 – textures of the metamorphic granulites from Blanche Marie; **a)** transmitted light, biotitesillimanite gneiss MKS 40 (Kabalebo) with clear leucosomes showing open folding; **b)** transmitted light, compositional banding in biotite-garnet gneiss MKS 49; **c)** transmitted light, example of a coarse-grained mafic granulite (MKS 43). The two lighter coloured bands are due to the local absence of hornblende; **d)** transmitted light, fine-grained mafic granulite (MKS 44). Note the similarity to figure 4.7b; **e)** XPL, sigmoidal inclusion patterns in a zoned plagioclase phenocryst from the leucosome in sample MKS 47 indicating synkinematic growth; **f)** PPL, reaction rim of pyroxene replacing hornblende which is indicative of prograde metamorphism (MKS 51).

Sample MKS 52 derived from the drill core was interpreted to be a discordant band and hence an example of the synkinematic metadolerite dikes typical for the Bakhuis horst *(see section 2.1.2).* Petrography of this sample did not confirm this interpretation: the texture was equigranular and identical to fine-grained sample MKS 44; no euhedral plagioclase phenocrysts were present.

4.2.1.2 intermediate granulites

The intermediate granulites (samples MKS 45, 46, 47, 48, 49, 50, 54 and 55) represent quartzofeldspatic orthopyroxene-bearing gneisses. The presence of quartz and alkali-feldspar and lower amount of mafic minerals compared to the mafic granulites forms the prime distinction. The intermediate samples all contain orthopyroxene in variable amounts. Clinopyroxene and hornblende are abundant in some samples but absent from others.

Garnet-bearing sample MKS 47 consists for more than half of a felsic leucosome. This leucosome contains large (>0.5 cm) quartz, alkali-feldspar, plagioclase and orthopyroxene grains. The presence of orthopyroxene suggests migmatisation under granulite-facies conditions. Multiple plagioclase grains in the leucosome contain sigmoidal inclusion patterns, indicative of synkinematic of growth of plagioclase *(see figure 4.11e)*. MKS 49 is a garnet-biotite gneiss that consists of felsic and more mafic bands *(see figure 4.11b)*. The mafic bands comprise abundant anhedral, highly deformed garnet and biotite. Orthoand clinopyroxene are present as well, together with subordinate greyish-blue to green hornblende that formed at the cost of pyroxene. This samples was taken near a sillimanite-bearing band.

The intermediate granulites are distinguished from the charnockites by the lack of euhedral plagioclase phenocrysts. Plagioclase in the granulites lacks zoning and Karlsbad twinning, two features typical of magmatic grains. Moreover, alkali-feldspar is much less abundant in the intermediate granulites than in the igneous charnockites. The most important discrimination however, is based on field evidence: the granulites are characterised by ubiquitous compositional banding while the charnockites form homogeneous outcrops.

4.2.1.3 Sample MKS 56

MKS 56 is a very felsic sample that does not contain any hornblende, ortho- nor clinopyroxene. The only mafic mineral present is biotite. It is taken from drill core LA 156 where it formed a 10-20 cm thick band or vein in a massive sequence of mafic granulite. Quartz is copious and the occurrence of large (up to 0.7cm) sub- to euhedral antiperthitic plagioclase and perthitic alkali-feldspar grains is typical for this sample. It resembles the leucosome part of MKS 47 but lacks the large orthopyroxene grains. Nevertheless, this sample is interpreted to represent a leucosome.

4.2.2 Sillimanite-gneiss from Kabalebo

The northernmost sampled outcrop along the Kabalebo river consists of an isolated patch of sillimanite gneiss. It is situated in the middle of the river and measures approximately 7 by 7 metres. This outcrop was sampled (MKS 40) because it provides an excellent example of a metapelitic gneiss. The sample contains two highly different generations of sillimanite *(see figure 4.12)*. Acicular sillimanite crystals and fine-grained biotite form pseudomorphs after a short prismatic mineral, which is considered to be cordierite *(see figure 4.12a,b)*. A second generation is formed by large (up to 3mm), short primatic coarse-grained sillimanite *(see figure 4.12c,d)*. The coarse sillimanite has grown during peak temperature metamorphic conditions, while the replacement of cordierite by sillimanite plus biotite is a retrograde feature. MKS 40 does not contain any orthopyroxene and therefore not the characteristic UHT-assemblage orthopyroxene-sillimanite-quartz, but a large part of the older, coarse metamorphic assemblage has been recrystallised. The pelitic gneiss has experienced migmatisation as is witnessed by the presence of large, folded leucosomes visible on the outcrop and thin section scale *(see figure 4.11a)*. One of these felsic layers contains an approximately 1 centimetre long mesoperthite grain with exsolution in the form of blocky patches. This mesoperthite is depicted on the title page of this thesis.



Figure 4.12 – sillimanite in sil-bt-gneiss MKS 40 (Kabalebo); **a)** PPL, pseudormorph after rectangular cordierite of acicular sillimanite crystals and fine-grained biotite; **b)** XPL, the same as a); **c)** PPL, coarse sillimanite grain surrounded by much finer-grained acicular sillimanite and biotite; **d)** XPL, the same as c).

4.3 – Summary

The Bakhuis charnockites have an undisputedly igneous origin. On the sample and outcrop scale, the charnockites are very homogeneous: compositional banding is non-existent. The consistent presence of euhedral plagioclase crystals that exhibit zoning and Karlsbad twinning forms another argument for an igneous origin. In addition, several samples (e.g. MKS 25 and 36) appear enriched in plagioclase and zircon by crystal accumulation, which is not compatible with metamorphic recrystallisation. Although a large part of the charnockite sample series has suffered intense deformation and obliteration of magmatic textures, multiple excellent examples remain. Petrography of the least deformed charnockites suggests high crystallisation temperatures probably above 900 °C on the basis of the presence of mesoperthitic exsolution in feldspar. The occurrence of inverted pigeonite in one of the samples is indicative of temperatures exceeding 950 °C.

Field evidence did not provide the desired clarity on the relationship between the charnockites and the metamorphic granulites; the two suites are never seen in direct contact with each other. However, the occurrence of banded mafic granulite xenoliths suggests that the charnockites are intrusive in the granulites. Moreover, the presence of a foliation in these xenoliths that is lacking in the charnockites indicates that these xenoliths underwent an older metamorphic event.

Coarse- and medium-grained mafic lithologies are present in or adjoining the charnockites as discrete xenoliths (<1.5 m) and larger, poorly constrained bodies. Both are characterised by an ophitic texture and the ubiquity of hornblende that distinguishes them from previously documented doleritic intrusives. Field relationships suggest that the charnockites are intrusive in these metadolerites and hence postdate them. However, it can not be excluded that the xenoliths represent mafic enclaves and formed contemporaneously with the charnockite magmatism.

Chapter 5 – whole rock geochemistry

In addition to the field relationships discussed in the preceding chapter, whole rock geochemical analysis of both the charnockites and the metamorphic suite is vital in establishing a genetic link between the two. In particular trace elements and radiogenic isotopes have the power to track magmatic processes that lead to the generation of the charnockitic magma and potentially distinguish between potential sources. Major and trace elements can also be used to characterise the processes occurring during crystallisation and evolution of a melt and therefore provide information on the petrogenesis of the charnockites. Moreover, the whole rock geochemistry of the Bakhuis belt will be compared to other charnockite occurrences and their typical composition to address potential differences between them.

In total, 39 samples were analysed for major and minor element concentrations with the XRF *(see sections 3.2.2 and 3.3.1)*, of which 21 magmatic charnockites, 16 granulites and 2 mafic igneous outliers. A selection of 21 samples (10 charnockites, 9 granulites and the two mafic outliers) was also processed for trace element analysis with ICP-MS and Sr-Nd isotope composition using TIMS *(see sections 3.2.3, 3.2.4, 3.2.5, 3.3.2 and 3.3.4)*. Tables containing the whole rock data are provided in appendix 2.1-2.5.

5.1 – Major element characteristics

Major element variation for the charnockites and granulites is depicted in Harker-style variation diagrams of the oxides versus silica in figure 5.2. The charnockites have a SiO_2 -content roughly between 55 and 73 wt%. The bulk of the samples plots above 65 wt% silica. Four intermediate outliers are present; three with silica-contents around 55 wt% and one at 61 wt%. For calcium and magnesium, the charnockites define a narrow compositional trend, while for most other elements the trend displays increased scatter. In the case of sodium, a clear trend can hardly be discerned and the data plot in a cloud of scatter. The

group of four intermediate samples behaves somewhat differently. In some cases (e.g. CaO), they plot in the array defined by the other charnockites, but for other elements (e.g. TiO_2 , Al_2O_3) they diverge from the main trend and show large variation within the group. The major element concentrations of the charnockites decrease with increasing silica-content for most elements while sodium is approximately constant. Potassium is the only exception as it drastically increases with silica.

In general, the granulites fall within the compositional range defined by the charnockite trends. The mafic granulites (<55 wt% SiO₂) however, display large compositional heterogeneity for elements such as FeO*, MgO and Al₂O₃. For these and other elements, they can not easily be linked to the charnockite suite. The most conspicuous discrepancy between the granulites and charnockites however, is formed by potassium. For this element, the two suites define highly contrasting trends. The granulites follow a subhorizontal array at less than 1 wt% K₂O while potassium-content in the charnockites increases from ~ 1.5 wt% for the intermediate group to over 5 wt% for the most felsic samples. One granulite sample is distinctive for multiple elements but particularly for Al₂O₃ and CaO. This is the metapelitic sillimanite gneiss sampled in the Kabalebo area. The two mafic outliers (the metadolerite from the Misty Mountain waterfall and the metagabbro sampled at Moi-Moi) are similar to each other with respect to major element concentrations except for CaO and FeO*. The metadolerite has a higher FeO* and lower calcium-content, the metagabbro vice versa. Both are compositionally indistinguishable from the mafic granulites.



Figure 5.1 – legend for all figures in this chapter. Filled symbols indicate samples analysed for major and trace elements plus Sr-Nd isotopes, open symbols only analysed for major elements. Blue diamonds: charnockites (dark blue for zircon samples); red square: metadolerite; red plus: metagabbro; green triangles: metamorphic granulites.



Figure 5.2 – Whole rock major element variation Harker-style diagrams. All concentrations are in weight percent (wt%) of the oxide, normalised to 100%. Iron is reported as total ferrous iron: FeO*. Symbols as in figure 5.1.



Figure 5.3 – major element variation. Symbols according to figure 5.1; **a)** P_2O_5 versus SiO_2 wt% for the charnockite samples. Apatite saturation isotherms (Harrison and Watson, 1984) have been plotted for reference. Most samples plot between 900 and 1000 °C. Note the anomalous behaviour of the four intermediate samples; **b)** magnesium number (Mg#) versus silica-content. Mg# is calculated as molar Mg / (Mg + Fe), assuming all iron is ferrous; **c)** aluminium saturation index (ASI) versus silica. Note the break in scale and the extreme peraluminosity of the sillimanite gneiss (MKS 40). ASI is calculated as molar Al / (Na + K + Ca).

In figure 5.3, the P_2O_5 -content is plotted against silica for the charnockite samples. Most samples plot between the 900 and 1000 °C apatite saturation isotherms (*Harrison and Watson, 1984*) and form a coherent trend. The four intermediate samples plot horizontally away from the main trend at the same phosphorous content as the 65 wt% SiO₂ charnockites. The magnesium number (molar Mg / (Mg+Fe)) for all samples decreases steadily with silica from around 70 for some mafic granulites to just under 20 for the most felsic charnockite samples (*see figure 5.3b*). The aluminium saturation index predicts in which phases aluminium will reside. Rocks with an ASI above unity are named peraluminous. This indicates that there is insufficient Ca, Na and K available to incorporate all aluminium in feldspar and that Al has to be allocated to other minerals such as micas. For highly peraluminous granitoid melts, even the micas are not sufficient and an Al-rich phase such as garnet might be present. The Bakhuis samples display a positive correlation between aluminium saturation index and silica (*see figure 5.3c*). The majority of the samples is metaluminous, but the most felsic charnockites are weakly peraluminous. A notable exception is metapelite sample MKS 40 (the sillimanite gneiss from the Kabalebo river), which is highly peraluminous.



Figure 5.4 – *QAP-diagram (e.g. Streckeisen, 1976) for the Bakhuis samples using CIPW normative abundances. Symbols according to figure 5.1.*

A CIPW norm was calculated for all samples *(see appendix 2.2)* according to the method described in Winter *(2001)*. Normative quartz, plagioclase and alkali-feldspar proportions are plotted in a QAP-diagram to allow distinction of different rock types. The charnockites plot in a tight compositional array on the boundary of the granodiorite and granite fields. The four compositional outliers are relatively silica-poor and plot towards lower quartz-normative concentrations in the quartz monzodiorite and diorite field. In contrast, the distinctive trends in the K_2O vs SiO₂ diagram *(see figure 5.2)* translate into a different granulite compositional array in the QAP-diagram as well. As a result of the lower potassium-content of the granulites, they contain less normative alkali-feldspar and hence plot in the quartz-diorite, tonalite and alkali-feldspar poor part of the granodiorite fields. As a notable exception, the metapelite plots on the granite-granodiorite field boundary. The mafic granulites, metadolerite and metagabbro are olivine-normative and therefore plot on the alkali-feldspar – plagioclase tieline. However, no olivine was encountered in these samples. As can be expected from the aluminium saturation index, the peraluminous samples are corundum-normative rather than diopside-normative.

When the samples are plotted in an alkalis-FeO-MgO (AFM) diagram *(see figure 5.5)*, the charnockites and more felsic granulites follow a calc-alkaline trend. The mafic granulites, metadolerite and metagabbro display much more scatter and range from calc-alkaline to tholeiitic. The amount of variation for these samples is surprising but in agreement with the variation seen in the Harker-diagrams *(see figure 5.2)*. In general, the entire sample suite tends towards calc-alkaline as highly ferroan compositions do not occur.



Figure 5.5 – AFM (alkalis-iron-magnesium) plot of the Bakhuis sample suite using concentrations in weight percent and assuming that all iron is ferrous. Tholeiitic – calc-alkaline divide after Irvine and Baragar (1971). Symbols according to figure 5.1.

5.2 – Trace element variation

For the discussion on trace element characteristics, the elements have been grouped based on their chemical behaviour. The incompatible large ion lithophile (LILE) and high field strength (HFSE) elements are discussed separately, as are the rare earth elements (REE) and compatible elements. Each group of trace elements has its specific merits and weaknesses but all can be of use in illuminating the petrogenetic history of the Bakhuis charnockites.

5.2.1 Large ion lithophile elements

The large ion lithophile elements (LILE) are a group of trace elements characterised by low charge to ionic radius ratios. Mono- and divalent alkali and alkaline-earth metals such as rubidium, strontium, barium and caesium are prime members of the LILE-group, but divalent europium and lead are also classified as LIL elements. Though generally incompatible due to their large ionic radii, LILE are incorporated into major silicate phases. Rubidium readily substitutes for potassium in alkali-feldspar, micas and to a lesser extent in hornblende. Barium is concentrated in alkali-feldspar to such an extent that it forms a solid solution from celsian ($Ba_2Al_2Si_2O_8$) to alkali-feldspar. Strontium and Eu²⁺ on the

other hand prefer the plagioclase lattice over alkali-feldspar and hornblende. The large ion lithophile elements can therefore be used to monitor fractional crystallisation of these phases. A major disadvantage of the LILE is that they can be highly mobile in fluids and are potentially lost from a sample during weathering or high-grade metamorphism. Results derived from LIL elements for rocks with a long history such as the Bakhuis charnockites and granulites should therefore be regarded with caution.



Figure 5.6 – variation diagrams for the large ion lithophile elements (LILE) plotted against silica. The Rb-Sr covariation is also displayed. Concentrations for elements in these graphs have been measured with the XRF on pressed powder pellets, except for europium that was measured by ICP-MS. Eu/Eu* is Eu / $\sqrt{(Sm_N \times Gd_N)}$. Symbols according to figure 5.1.

Variation in large ion lithophile element concentration versus SiO₂-content for all samples is displayed in figure 5.6. The LIL elements are characterised by increased scatter compared to the major elements. Barium in particular does not correlate with silica-content but forms a data cloud. Rubidium behaves similar to potassium and it is characterised by the same dichotomy between charnockites and granulites. The charnockites have Rb-concentrations increasing from about 30 to 120 ppm with increasing SiO₂ while the granulites contain on average less than 30 ppm Rb. Two felsic samples from Misty Mountain have anomalously high Rb-contents in excess of 200 ppm. All mafic granulites plus the two igneous gabbroic rocks contain less than 10 ppm Rb. Strontium decreases with silica and the charnockites contain consistently more Sr than the granulites. One of the four charnockites with an intermediate silicacomposition contains nearly 1000 ppm strontium. This is sample MKS 36 that is characterised by a cumulate texture in respect to plagioclase. Since Sr is compatible in plagioclase, the high Sr-concentration corroborates this petrographic observation. The mafic rocks show variable Sr-concentrations, as does the group of four intermediate charnockites. Rubidium is negatively correlated with strontium concentration. Barium concentrations for the metamorphic suite are generally <500 ppm while the charnockites contain 700-2500 ppm Ba. There is no obvious correlation between barium and silica content. Most samples have a weakly negative europium-anomaly, but three charnockite samples are characterised by large positive anomalies that can not be correlated to SiO₂. Finally, the Ba/Sr ratio is less than 2 for the metamorphic suite, but increases up to 9 with increasing silica-content for the charnockites.

5.2.2 High field strength elements

Similar to the LILE, high field strength elements (HFSE) are generally incompatible during mantle and crustal melting. Their incompatibility is caused by a high charge (3+ or more) and small ionic radius, which makes them difficult to incorporate in the crystals lattice of major silicate minerals. The HFSE are therefore concentrated in accessory phases. This implies that, if these phases are residual during melting, the resulting melt can be severely HFSE depleted. Zirconium, hafnium, niobium, tantalum and titanium are important members of the HFSE group, but the rare earth elements, uranium and thorium are also often included. A marked difference with the large ion lithophile elements is that the HFSE are highly immobile in fluids or during metamorphism. They are therefore likely to remain undisturbed even during high grade metamorphism. Common accessory minerals that govern the high field strength element budget are zircon and Ti-rich phases such as rutile and titanite.

Figure 5.7 displays variation diagrams of a selection of high field strength elements versus silica-content. The general trend is that the HFSE are more concentrated in the charnockites compared to the metamorphic granulites. Niobium and tantalum are geochemical twins that behave very similarly. This is reflected in their mutual decrease with increasing silica-content. Sample MKS 38 with a SiO₂-concentration of 61 wt% is enriched in Nb and Ta relative to the other charnockites. The mafic granulites and two gabbroic rocks have low and consistent Nb-Ta concentrations. One sample displays a spurious tantalum-concentration of almost 15 ppm compared to the average 1 ppm for other samples while Nb shows no evidence for enrichment. Such extreme Nb-Ta fractionation is impossible to achieve in nature and the Ta-anomaly is probably caused by analytical error.

Zirconium and hafnium concentrations are high compared to normal granitoids and show an overall decrease with silica. Similar to Nb and Ta, these two elements are geochemically identical. They are highly incompatible in most phases but do form their own mineral: zircon. Three samples are characterised by joined increased Zr-Hf content; one of these is MKS 36 that appears enriched in zircon and has a very high Zr-content of 1400 ppm. In contrast, the other two intermediate charnockites contain less than average zirconium and hafnium. The granulites have low and invariable Zr-Hf concentrations. The Zr/Hf ratio of the charnockites shows a weak negative correlation with SiO_2 and is different to the granulites. Cerium-concentration is also correlated with silica and higher in the charnockites compared to the metamorphic suite.

Uranium and thorium are often incorporated in the HFSE-group, but have one marked difference: they can both be highly mobile in certain fluids and can therefore be lost from during high-grade metamorphism. Concentrations for both elements are very low compared to average granite and they are not correlated to silica-content. The low U-Th abundances are discussed further in section 5.2.5.



Figure 5.7 (previous page) – variation diagrams for the high field strength elements (HFSE) concentrations versus silica. All elements are measured by ICP-MS with exception of Nb and Zr, which are measured by XRF. Note the break in scale for the Ta-SiO₂ diagram. Symbols according to figure 5.1.

5.2.3 Compatible elements

Compatible elements prefer the solid over the liquid phase during melting and crystallisation. This means that they are concentrated in residues and cumulates of early fractionation products and are therefore quickly lost from an evolving magma. High concentrations of compatible elements such as nickel, chromium, cobalt and vanadium indicate either a large contribution from the mantle, accumulation of mafic phases or a melt that has experienced very little evolution. Ni and Co are preferentially incorporated in olivine, while Cr prefers pyroxene and vanadium Ti-rich phases.

Concentrations and variations in compatible elements are depicted in figure 5.8. In accordance to the description above, the compatible elements nickel, chromium and vanadium are concentrated in the mafic granulites and two gabbroic samples. Concentrations of these elements steeply decrease with silicacontent for the charnockites and intermediate granulites. Of the four intermediate charnockite samples, two (MKS 36 and 38) plot consistently below the general trend, while the other two plot between the charnockites and the mafic granulites. The element chromium is slightly more concentrated in the intermediate granulites relative to the main charnockite trend. Cobalt variation is not displayed but mirrors the behaviour of the geochemically similar element nickel.

Gallium behaves differently compared to the other three elements. Plotting below aluminium in the periodic table, its small ionic radius of 0.055 nm (Shannon, 1976) and valence of 3 + predict that it should be highly compatible. The Ga-concentration of the mafic samples is however, lower than the more felsic rocks. The charnockites do display a strong negative correlation between Ga and SiO₂.



Figure 5.8 – variation diagrams for compatible elements versus silica-content. Nickel and gallium concentrations have been measured by ICP-MS; chromium and vanadium by XRF. Note the log-scale for the Ni and Cr diagrams. Symbols according to figure 5.1.

5.2.4 Rare earth elements

The rare earth elements (REE) or lanthanides are a group of elements ranging from lanthanum to lutetium. They are characterised by highly similar geochemical and physical properties and therefore behave as a coherent group. All rare earth elements are trivalent ions, with the exception of cerium and europium, which can be tetravalent and divalent respectively under the appropriate oxygen fugacities. The ionic radius of the REE decreases steadily from La to Lu: the so-called lanthanide contraction. As smaller ions with a similar charge are preferentially incorporated in a solid phase, incompatibility of the rare earth elements decreases with atomic number. This systematic decrease in incompatibility from lanthanum to lutetium allows the applications of the REE in a myriad of petrogenetic modelling scenarios. Trivalent yttrium has an ionic radius that is almost identical to the rare earth element holmium and is therefore sometimes included in the REE. Promethium (Pm) is not naturally occurring and not analysed, but it is included in figure 5.9 to prevent a strange kink in the REE-curve.

Since elements with an even atomic number are more abundant in nature than odd-numbered elements, the Oddo-Harkins effect, simply plotting the REE against their concentration will result in a saw-tooth shaped graph. To eliminate this effect, rare earth element concentrations are normalised to a common reference standard. CI chondrite is most frequently used as normalisation factor and allows direct comparison of REEconcentrations to bulk Earth. In this thesis, normalising values from McDonough and Sun (1995) are used and the subscript "N" denotes chondrite normalised values.

The trivalent rare earth elements are generally incompatible in major silicate minerals and their budget is primarily governed by accessory phases. These minor phases however favour certain subgroups within the rare-earth elements. Garnet and zircon for instance preferentially incorporate the heavy REE (Er-Lu) over light REE (La-Nd). Hornblende and titanite include the middle REE (Sm-Ho) while e.g. apatite favours the REE.

Figure 5.9 – REE variation diagrams for the Bakhuis samples. REE concentrations have been normalised to CI chondrite (McDonough and Sun, 1995). Anomalous samples have been indicated.





Figure 5.10 – rare earth element variation diagrams depicting the total REE concentration (Σ REE) versus silicacontent and the slopes of the HREE, LREE and total REE versus a REE-concentration. Note the log-scale for the (La/Yb)_N vs. Yb_N plot. All concentrations measured by ICP-MS. The subscript "N" denotes normalisation to CI chrondrite (McDonough and Sun, 1995). Symbols according to figure 5.1.

The Bakhuis charnockites show heterogeneous rare earth patterns *(see figure 5.9).* A main trend is defined by 8 samples with a total REE-slope $((La/Yb)_N)$ of ~9 at a normalised ytterbium concentration of around 22 *(see figure 5.10).* Two samples from this main group have anomalously large positive europium anomalies *(see also figure 5.6),* and sample MKS 30 is characterised by a lower LREE-slope $((La/Sm)_N)$. Of the three outliers, samples MKS 19 and 38 have a similar REE-slope but respectively lower and higher than average REE concentrations. Sample MKS 26 has both a steeper REE-slope, much lower absolute rare earth element concentrations and a large Eu/Eu* of 2.22. As is evident from the ΣREE vs. SiO₂ diagram, REE-concentrations decrease with increasing silica-content. The slope of the light REE is negatively correlated with Sm_N and hence increases with SiO₂. For the heavy REE, no correlation between slope and concentration is witnessed.

In the case of the metamorphic suite, the distinction of mafic and intermediate granulites made on the basis of petrography *(see section 4.2)* is also discernible in the $(La/Sm)_N$ vs. Sm_N diagram. The mafic granulites are characterised by both lower LREE-slopes and absolute samarium concentration relative to the intermediate granulites that plot at a constant Sm_N of ~40. One mafic sample has a positive LREE slope, indicated by the sub-unity $(La/Sm)_N$ ratio. The highly siliceous sample MKS 56 has a distinct REEpattern. Its total REE-concentration is very low, but the parabolic curve is most conspicuous. MKS 56 has a positive heavy REE slope ($(Er/Lu)_N \approx 0.6$) and a steep, negative light REE slope, which results in a minimum at dysprosium-holmium. The two gabbroic magmatic rocks from the Kabalebo area have different REE-patterns. The metadolerite (MKS 32) has an essentially flat slope in contrast to the metagabbro (MKS 37) and a higher heavy REE-content. Both are indistinguishable from the mafic granulites based on rare earth element characteristics. A comparison of rare earth patterns between the charnockites and metamorphic suite indicates that the charnockites have overall higher REE-concentrations. As can be seen in figure 5.10, they can also effectively be separated in the total REE-slope vs. Yb_N diagram. The granulites are characterised by consistently lower (La/Yb)_N at a given Yb_N compared to the charnockites.

5.2.5 Multi-element variation diagrams

Multi-element variation diagrams, also known as spider diagrams, are basically extended rare earth element plots. By placing the element in order of increasing incompatibility and normalising to a reference value, samples can be easily compared and relative enrichment or depletion in elements are visible as peaks in the diagram. In figure 5.11, primitive mantle normalised *(Sun and McDonough, 1989)* multi-element variation diagrams for the Bakhuis samples are shown.

In the ideal situation of melting of primitive mantle, normalised trace element concentrations of the resulting melts should increase steadily from ytterbium to caesium. As is evident from figure 5.11 however, multiple elements are not in accordance with this generalisation. All groups (charnockites, metamorphic and the gabbroic rocks) are characterised by a pronounced negative anomaly at niobium-tantalum. Other high field strength elements such as titanium display less systematic negative peaks. At the same time, most incompatible elements are highly enriched compared to primitive mantle. The low Nb-Ta-(HFSE) concentrations are therefore not likely produced by melt depletion since that would imply that other incompatible elements would also be depleted. This decoupling between HFSE and large ion lithophile elements is a characteristic feature of a subduction zone setting. HFSE are preferentially held back in accessory phases (e.g. rutile) present in the subducting slab or mantle wedge while LILE enter the mantle wedge upon dehydration of the slab and are incorporated into the arc melts. A positive lead anomaly is also an indication of a subduction zone environment. This Pb-anomaly is a ubiquitous feature of the charnockites, but is only sparsely present in the granulites.

A very conspicuous feature of the Bakhuis samples is the prominent negative uranium±thorium anomaly. In particular the charnockites have a large, negative U-Th anomaly. The anomaly is less pronounced for the two gabbroic samples but still recognisable. The granulites have a systematic deficit in uranium, but variable Th-depletion. Both uranium and thorium can be mobile in certain fluids and could potentially be lost from a rock during metamorphic dehydration *(see section 7.1 for a more comprehensive discussion)*. A negative U-Th anomaly is a typical feature of granulite terrains worldwide *(e.g. Rudnick and Presper, 1990)*. Other highly mobile elements such as the alkalis (potassium, rubidium and caesium) are also relatively low for the metamorphic suite. Their depletion is less intense for the charnockites but still the alkali-concentrations are below expectation.

Normalised abundances of the geochemical twins zirconium and hafnium are highly variable in the charnockites and these elements exhibit both positive and negative Zr-Hf anomalies. This is consistent with their large variation with silica-content (see figure 5.7) and the sample with the highest absolute Zr-Hf abundance and highest positive anomaly is MKS 36.

When the three groups are compared, the same overall conclusions are reached as for the rare earth element variation. The charnockites contain on average more trace elements than the granulites and gabbroic rocks. The mafic granulites and gabbroic samples are variable but indistinguishable from each other. All samples are characterised by a decoupled HFSE-LILE pattern typical for a subduction zone environment and mobile element (Cs, Rb, U, Th) depletion.

Figure 5.11 (next page) – multi-element variation diagrams for the Bakhuis sample suite. The elements have been ordered so that incompatibility decreases from left to right. Trace element concentrations have been normalised to primitive mantle values. Element order and normalising values according to Sun and McDonough (1989).





Figure 5.12 – Zr-Y-Ti tectonic discrimination diagram for basaltic rocks after Pearce and Cann (1973). The two gabbroic samples and mafic granulites have been plotted. Symbols according to figure 5.1. Elemental concentrations are in ppm; plotting coordinates for the field boundaries after Rollinson (1993). WPB: withinplate basalt; IAT: island-arc tholeiite; MORB: mid-ocean ridge basalt; CAB: calc-alkaline basalt

5.2.6 Trace element discrimination diagrams

Plotting of large datasets of samples has revealed that distinct trace element ratios or concentrations correlate empirically with different tectonic environments. In theory, certain trace elements could be used to infer the original tectonic setting for old or highly deformed rocks. Many tectonic discrimination diagrams have been developed with variable degrees of usefulness.

Figure 5.12 and 5.13 are examples of three of the more commonly used discrimination diagrams for basaltic and granitic rocks respectively. These diagrams were selected because: i) they are among the best constrained diagrams available and are supported by a large database of samples from a range of



Figure 5.13 – tectonic discrimination diagrams for granites applied to the charnockites and intermediate granulites. Symbols as in figure 5.1. VAG: volcanic-arc granites, syn-COLG: syn-collisional granites, WPG: withinplate granites, ORG: ocean-ridge granites. Plotting coordinates for field boundaries after Rollinson (1993); **a**) Y-Nb discrimination diagram after Pearce et. al. (1984). The dashed line separates within-plate granites from anomalous ridges; **b**) Rb-(Y+Nb) discrimination diagram after Pearce et. al. (1984).
localities; and ii) they make use of trace elements that can be considered to be immobile during metamorphism and weathering. Tectonic discrimination diagrams are of course oversimplifications that do not take processes such as fractional crystallisation and assimilation into account. Especially for granitic rocks, fractionation of accessory phases can have significant effects on the location of samples in a discrimination diagram. Therefore, these type of diagrams should not be regarded as proof for a particular tectonic setting by itself but rather as a corroboration of other lines of evidence. Furthermore, they should not be applied to single samples but preferably to large sample suites. The Zr-Y-Ti discrimination diagram for basaltic rocks (*Pearce and Cann, 1973*) with the mafic granulites and gabbroic rocks is displayed in figure 5.12. Most samples plot in the island-arc tholeiite (IAT) and IAT-MORB field. This is in general agreement with the weakly tholeiitic trend of the mafic samples seen in the AFM diagram (see figure 5.5). One sample plots clearly in the calk-alkaline field (CAB) while the metagabbro plots outside any of the fields. It is impossible to distinguish between island-arc tholeiites and mid-ocean ridge basalt (MORB) in the Zr-Y-Ti diagram. Plotting of yttrium versus chromium concentrations does allow effective discrimination between these two settings (*Pearce, 1982*). In such a diagram, all mafic samples plot in the island-arc tholeiite field (not shown).

The charnockites and intermediate granulites have been plotted in two discrimination diagrams for granitic rocks *(see figure 5.13).* Most significance should be paid to the Nb-Y diagram, since the mobility of rubidium potentially leads to spurious results in the Rb-(Y+Nb) diagram. Despite this, the two diagrams are in good agreement with each other. The intermediate granulites plot firmly in the syn-collisional (syn-COLG) and volcanic arc (VAG) granite field in the Nb-Y diagram, but straddle the boundary with ocean-ridge granites in the Rb-(Y+Nb) diagram. The latter diagram does separate the VAG and syn-COLG fields and the granulites plot as volcanic arc granites. Preferential loss of rubidium however, will cause migration away from the syn-COLG field. The charnockites cluster around the VAG and within-plate granite (WPG) field boundary in both diagrams, which is in line with the subduction zone signature witnessed by the negative Nb-Ta anomaly. There is no obvious relationship between silica-content of the samples and their location in any of the diagrams.

A method of distinguishing the source of a suite of igneous rocks is using the ratio of a pair of highly incompatible trace elements. In theory, incompatible elements with similar distribution coefficients will not be fractionated during partial melting and fractional crystallisation. Ratios of these elements can therefore be used as a proxy for the composition of the source rocks. This approach works best for mafic, juvenile rocks. Accessory phases that accommodate incompatible elements are not regarded to exert significant influence on the trace element behaviour during mantle melting. Moreover, mafic rocks tend to be less affected by fractionation of these accessory phases. For more evolved rock that potentially



Figure 5.14 – trace element ratio discrimination diagrams. Symbols as in figure 5.1 with the exception that mafic granulites are normal green triangles and intermediate granulites are inverted green triangles; **a**) Ce/Sr vs. Zr/Hf diagram; **b**) La/Nb vs. Eu/Ti diagram

formed by re-melting of crustal material, incompatible element rich phases in the residue can severely fractionate trace element ratios. Nevertheless, this approach was undertaken for the Bakhuis samples in an attempt to put constraints in the source of the charnockitic melt. As explained in section 5.2.5, the Bakhuis samples display evidence of variable loss of mobile elements (U, Th, K, Rb, Cs). These elements, although normally highly useful in source discrimination, were therefore avoided and emphasis was placed on the HFSE and REE. Multiple trace element pairs with similar incompatibility *(Sun and McDonough, 1989; Rollinson, 1993)* were studied. The four most relevant ratios have been plotted in figure 5.14. In figure 5.14a, the charnockites and intermediate granulites plot at significantly higher Ce/Sr and Zr/Hf compared to the mafic granulites and gabbroic rocks. For the charnockites, Ce/Sr is negatively correlated with Zr/Hf. The La/Nb vs. Eu/Ti diagram shows more scatter and no obvious separation between the two groups defined in the previous diagram. The relevance and implications of these diagrams will be discussed in detail in section 7.2.

5.3 – Radiogenic isotope composition

Radiogenic isotopes of for example strontium, neodymium, hafnium and lead constitute the most refined tool for magma source identification. The isotope composition of a rock or mineral (i.e. the ratio of a radiogenic isotope over a non-radiogenic isotope: for instance ¹⁴³Nd/¹⁴⁴Nd) is dependant on two parameters: the time-integrated parent-daughter ratio of the sample and time. Samples with e.g. a low Rb/Sr ratios contain little of the radioactive parent and will therefore experience little radiogenic ingrowth with time and have an unradiogenic strontium isotope composition. In contrast, samples with a high parent-daughter ratio experience increased ingrowth and have a more radiogenic isotope composition. This difference will become larger with time as the high parent/daughter sample will have more time for radiogenic ingrowth, while the isotope composition of the low parent/daughter sample will only increase slightly. An important implication is that these radiogenic isotopes therefore can be used as a absolute dating technique.

Additionally, isotopic fractionation is assumed to be non-existent in nature for elements with an atomic weight in the range of the regularly used isotopes mentioned above. Any petrogenetic process, although likely to fractionate the parent-daughter ratio, will therefore not alter the isotope composition. As a consequence, radiogenic isotopes provide a powerful tool to discriminate between potential magma sources.

The two radioactive decay systems employed in this thesis are the β -decay of rubidium-87 to strontium-87 with a half-live of 48.8 Gyr *(Steiger and Jäger, 1977)* and the α -decay of samarium-147 to neodymium-143 with a half-live of 106 Gyr *(Lugmair and Marti, 1978)*. The rubidium-strontium system is highly useful in crustal studies as both elements are incompatible and preferentially reside in the crust. Both are large ion lithophile elements and substitute for K and Ca respectively in major silicate phases. As rubidium is generally more incompatible than strontium, partial melting and fractional crystallisation tend to increase the Rb/Sr ratio of a melt. Hence, the crust is a major reservoir for radiogenic strontium. Since infracrustal differentiation effectively fractionates rubidium from strontium, this isotope system is ideal in tracking crustal processes. Its use however, is impeded by the mobility of these two elements. Metamorphism, hydrothermal alteration and weathering can severely disturb the Rb-Sr system, restricting its use to relatively unaltered sample suites.

Samarium and neodymium are rare earth elements and hence much less affected by metamorphism and alteration. Due to the coherent behaviour of the REE *(see section 5.2.4)*, the parent and daughter elements will not be highly fractionated during crustal processes. The Sm-Nd isotope system therefore has the ability to "see through" episodes of high-grade metamorphism and crustal differentiation and provide information on the original extraction from the mantle. Its behaviour is exactly opposite to the Rb-Sr system. As is evident from crustal rare earth patterns *(see figure 5.9)*, the parent element (samarium) is more compatible than the daughter. Melt evolution will therefore decrease the parentdaughter ratio leading to highly unradiogenic evolved melts; the present-day Nd-isotope composition of the crust is therefore less radiogenic than that of the mantle.

Neodymium isotope composition is often reported as epsilon-units (ϵ_{Nd}), which represents the deviation from the bulk Earth neodymium evolution chondritic uniform reservoir (CHUR). The epsilon-notation is calculated by:



Figure 5.15 – strontium-neodymium isotopes of the Bakhuis samples as measured by TIMS. Symbols according to figure 5.1; a) present-day Sr-Nd isotope composition. Error bars (2σ) are smaller than symbol size; b) Sr-Nd isotope composition corrected to an average intrusion age for the charnockites of 1975 Ma (see section 6.4). ⁸⁷Rb/⁸⁶Sr and ¹⁴⁷Sm/¹⁴⁴Nd ratios were calculated using XRF and ICP-MS data respectively, assuming a 3% error on Rb/Sr and 4% error on Sm/Nd (see sections 3.3.1 and 3.3.2). Error bars are 2σ.

$$\boldsymbol{\varepsilon}_{Nd(t)} = \left[\frac{({}^{143}Nd/{}^{144}Nd)_{sample(t)}}{({}^{143}Nd/{}^{144}Nd)_{CHUR(t)}} - 1\right] \times 10^4$$

The present-day CHUR values from Hamilton et. al. (1983) are used in this thesis: ¹⁴³Nd/¹⁴³Nd = 0.512638 and ¹⁴⁷Sm/¹⁴⁴Nd = 0.1966. Negative ε_{Nd} indicates unradiogenic neodymium compositions that are typical for the crust, positive designate radiogenic, depleted mantle sources. Due to the limited Sm-Nd fractionation in crustal processes, neodymium isotopes can be used to constrain the timing of original extraction from the mantle. Assuming a fixed evolution curve for the mantle, the intersection between this mantle growth curve and the evolution curve of a sample defined by its ¹⁴³Nd/¹⁴³Nd and ¹⁴⁷Sm/¹⁴⁴Nd ratios will yield a mantle extraction model age. Multiple mantle evolution models have been proposed for CHUR and depleted mantle (*Dickin, 2005*). In line with the recommendation from this author, the depleted mantle model by DePaolo (1981) was adopted in this research project. This model assumes a parabolic evolution of the depleted mantle and its ε_{Nd} is given by the equation: $\varepsilon_{Nd (T)} = 0.25T^2 - 3T + 8.5$; with time (T) in Gyr. Neodymium mantle model ages are reported as T_{DM} .

Isotopes compositions age-corrected to the time of crystallisation are called initial ratios. These are calculated using the present-day (i.e. measured) isotope composition and parent daughter ratio in combination with a presumed crystallisation age of the magma. All initial ratios reported in this thesis are calculated to an average intrusion age for the Bakhuis charnockites of 1975 Ma *(see section 6.4).* The decay constants of 1.42×10^{-11} for ⁸⁷Rb *(Steiger and Jäger, 1977)* and 6.54×10^{-12} for ¹⁴⁷Sm *(Lugmair and Marti, 1978)* are used. Recent work *(e.g. Begemann et. al., 2001)* has revealed a discrepancy in the rubidium decay constant of 1.408×10^{-11} is suggested by multiple studies *(Begemann et. al., 2001 and references therein)*, but this value has not been taken in common use. Therefore, the original decay constant recommended by Steiger and Jäger is adopted. XRF and ICP-MS derived concentrations of Rb-Sr and Sm-Nd respectively have been used to calculate ⁸⁷Rb/⁸⁶Sr and ¹⁴⁷Sm/¹⁴⁴Nd ratios. Errors on these concentrations are assumed to be 3% for Rb/Sr and 4% for Sm/Nd *(see sections 3.3.1 and 3.3.2).* Initial ratios are denoted by the subscript "i".

5.3.1 charnockite Rb-Sr and Sm-Nd geochronology

If a suite of samples with variable parent-daughter ratios crystallised from a magma with a homogenous isotope composition, their present day isotope ratios should plot on a straight line in an isotope composition versus parent-daughter ratio diagram. The slope of this line is only proportional to time. Hence, if the criteria of homogeneous initial ratio and closed system behaviour are met, such as diagram can be used to establish an age for the suite of samples. This isochron approach is most effective if there is little ambiguity on the criteria mentioned above and the samples show a large spread in parent-daughter ratios. A good example of this approach is the use of minerals from a single rock sample with hugely contrasting parent-daughter ratios. It is also possible to apply the isochron method to a suite of rocks that are assumed to be cogenetic and of equal age.

An isochron age for the Bakhuis charnockites (excluding the two gabbroic samples and all granulites) has been calculated for the Rb-Sr system using Isoplot 3.71 (Ludwig, 2008). This resulted in a rubidium-strontium age of 1867±42 Ma with an initial ratio of 0.70254 (see figure 5.16). The relatively low error on the isochron age is caused by the wide spread in ⁸⁷Rb/⁸⁶Sr ratios of the Bakhuis charnockites, which allows a confident calculation of an isochron regression. The MSWD is a measure of the amount of scatter in a regression (see section 6.4.1 for a more detailed explanation). Generally, a MSWD <2.5 is required to classify a regression as an isochron rather than an errorchron (Dickin, 2005). The Rb-Sr regression has a MSWD of 3.4, which technically does not justify its recognition as an isochron. However, the MSWD is low considering the fact that ⁸⁷Rb/⁸⁶Sr ratios were derived from XRF data rather than isotope dilution measurements. Nevertheless, the obtained Rb-Sr age is at odds with the zircon U-Pb ages presented in chapter 6. These highly precise ages cluster around 1975 Ma and are far outside error of the Rb-Sr isochron age. The difference between the U-Pb zircon and Rb-Sr isochron ages is probably caused by later-stage resetting of the Rb-Sr system while zircon remained closed. However, the resultant age of 1867±42 Ma does not correlate to any known geological event in the region. Mixing between two different rock suites does not appear plausible, as the five zircon samples themselves define an isochron with a similar age (see figure 5.16).



Figure 5.16 – Rb-Sr and Sm-Nd isochron diagrams for the Bakhuis charnockites. Symbols according to figure 5.1. Parent-daughter ratios have been calculated using XRF (Rb-Sr) and ICP-MS (Sm-Nd) data assuming 3% and 4% errors respectively. Error bars (20) are smaller than or equal to symbol size. The Rb-Sr system yields a good fit at an age of 1867±42 Ma and initial ⁸⁷Sr/⁸⁶Sr of 0.70254. Samarium-neodymium data do not fit an isochron. An errorchron age of 2122 Ma is obtained.

The samarium-neodymium data do not allow the calculation of an isochron age with Isoplot due the scatter of the data. This is partly caused by the small spread in ¹⁴⁷Sm/¹⁴⁴Nd ratios exhibited by the charnockite suite. A simple least-squares regression to the data yields a spurious age of 2122 Ma. Due to the degree of scatter and relatively large errors on the Sm/Nd ratio, this age can be assumed to be within error of the zircon U-Pb ages. Open system behaviour appears unlikely in the case of the relatively immobile rare earth elements. Isotope dilution analysis may be required to elucidate the inconsistent Rb-Sr and Sm-Nd ages.

5.3.2 Strontium-neodymium isotopic variation

Diagrams of radiogenic isotopes against SiO₂, each other and elemental abundances are displayed in figure 5.15 and 5.17. The first figure depicts the ⁸⁷Sr/⁸⁶Sr versus ε_{Nd} variation for both the present-day values and age corrected (1975 Ma) initial ratios. Variation of the initial ratios with silica-content is shown in figure 5.17. The granulites and charnockites can easily be distinguished based on their present-day Sr-Nd systematics. Present-day strontium isotope composition is highly variable for the charnockites; ⁸⁷Sr/⁸⁶Sr ranges from approximately 0.704 to 0.743. The spread in strontium isotope composition of the granulites and two gabbroic samples is much smaller; they cluster around a ⁸⁷Sr/⁸⁶Sr of 0.703. Two obvious outliers are present in the granulite suite *(see figure 5.15a)*. Both the sillimanite gneiss (MKS 40) and the abnormal leucosome sample (MKS 56) have significantly more radiogenic strontium compositions roughly at a ⁸⁷Sr/⁸⁶Sr of 0.735. The highly unradiogenic character of the granulites, they plot close to modern-day depleted mantle, is caused by their very low rubidium concentrations *(see figure 5.6)*. Despite the Proterozoic age of the samples, little radiogenic ingrowth has occurred.

As expected from the larger ¹⁴⁷Sm half-live and relatively small Sm-Nd fractionation in crustal processes, the spread in neodymium isotope composition for all samples is small. Neodymium systematics of the sample suite are exactly opposite to strontium. The charnockites define a narrow compositional range in ¹⁴³Nd/¹⁴⁴Nd between 0.5114 and 0.5118, corresponding to an ε_{Nd} value of about -20. The granulites on the other hand, have a much wider compositional range of ¹⁴³Nd/¹⁴⁴Nd ratios between 0.5112 and 0.5129 (ε_{Nd} values of approximately 5 to -28). Surprising is the positive present-day ε_{Nd} value for a Proterozoic crustal rock: mafic granulite MKS 42. This implies a superchondritic Sm/Nd ratio and hence a positive LREE slope. Another mafic granulite and the metadolerite also plot close to bulk Earth.

Initial ratios of the charnockites and granulites display much more similarity than the present-day values (see figure 5.15b). Mafic granulites MKS 44 and 51, the two gabbroic samples and several charnockite samples all plot within error of each other at an initial ${}^{87}Sr/{}^{86}Sr$ of 0.7023 and initial ϵ_{Nd} of about 1. Several charnockite samples are characterised by very low initial strontium isotope composition approaching the value of CHUR at the formation of the Earth and are associated with relatively large errors. Unless they are derived from a source that was depleted in rubidium shortly after the accretion of the Earth and hence suffered no radiogenic ingrowth, these low ratios are difficult to explain. As this is not a very plausible scenario, the most likely explanation again is resetting of the Rb-Sr after crystallisation. A general trend of decrease in initial ${}^{87}Sr/{}^{86}Sr$ ratio with increasing present-day ${}^{87}Sr/{}^{86}Sr$ ratios can be identified; as is to be expected from the difference in Rb-Sr isochron age and the U-Pb age used as initial age. The error on the initial ratio is predominantly governed by the magnitude of the Rb/Sr ratio of a sample and not by the error on the measured ${}^{87}Sr/{}^{86}Sr$ ratio. Therefore, the samples with the lowest Rb/Sr ratio are considered to be the best approximation of the charnockite initial ratios. These samples (e.g. MKS 25, 36, 38) consistently plot within error of the mafic granulites, dolerite and metagabbro.



Figure 5.17 – isotopic variation of the Bakhuis samples with silica-content and the reciprocal of the daughterelement concentrations. Initial ratios have been calculated assuming an intrusion age for the charnockites of 1975 Ma (see section 6.4); ⁸⁷Rb/⁸⁶Sr and ¹⁴⁷Sm/¹⁴⁴Nd ratios were derived from XRF and ICP-MS data respectively, assuming a 3% error on Rb/Sr and 4% error on Sm/Nd (see sections 3.3.1 and 3.3.2). Symbols according to figure 5.1. Error bars are 20.

Four granulites samples are characterised by initial 87 Sr/ 86 Sr ratios >0.7029, which is outside error of the group defined by the mafic granulites and gabbroic samples. These anomalously radiogenic samples are three intermediate granulites (MKS 45, 54 and 55) and the sillimanite gneiss (MKS 40). Their low Rb-concentrations lead to small errors on the age-corrected strontium ratios that therefore tend to be less equivocal than the charnockite samples with anomalously low initial Sr-isotope composition. Accordingly, it can be concluded that these intermediate granulites have a significantly different initial strontium isotope composition than the charnockites, mafic granulites and gabbroic samples. All samples except the anomalous leucosome (MKS 56) have identical initial ϵ_{Nd} values.

This conclusion based on figure 5.15 is supported by figure 5.17. The intermediate granulites have an initial ⁸⁷Sr/⁸⁶Sr that is higher than and outside error of the other lithologies. In the diagram of initial isotope ¹⁴³Nd/¹⁴⁴Nd versus silica-content, all the samples plot within error of each other. Nevertheless, there appears to be a negative correlation between the two parameters for the granulites. This graph suggests that the more felsic granulites suffered less radiogenic ingrowth than the mafic granulites since their extraction from the mantle. The relatively small difference however, does indicate that extraction from the mantle did not precede 1975 Ma by a large amount of time. A more detailed discussion on granulite protolith formation is offered in the next paragraph.

Plotting initial ratios of a radiogenic isotope against the reciprocal of the concentration of the daughter element (see figure 5.17) can potentially reveal different source rocks. Binary mixing of two components will define a straight line on such a diagram. For the Bakhuis sample suite, no evidence is found for mixing of two or multiple sources. For neodymium, the mafic granulites and gabbroic samples are clearly distinguishable from the intermediate granulites and charnockites based on the neodymium content.

5.3.3 Neodymium model ages

An important objective of the isotope study was to assess whether an Archaean component is present in the Bakhuis charnockites. As explained above, neodymium model ages can provide valuable information on the timing of original extraction from the mantle even for high-grade metamorphic or re-melted granitoid rocks. Neodymium model ages ($T_{\rm DM}$) have been calculated for the Bakhuis samples according to the mantle evolution model by DePaolo (1981), and the results are plotted against silica-content in figure 5.18. The charnockite $T_{\rm DM}$ ages cluster tightly around approximately 2.3 Ga. The granulites display



Figure 5.18 – neodymium model ages for the Bakhuis samples calculated according to the depleted mantle evolution model by DePaolo (1981). Error bars have been omitted for the sake of clarity but are on average 150 Myr for the felsic (>55 wt% SiO₂) samples and 250 Myr for the mafic rocks. Symbols according to figure 5.1.

increased scatter but all plot between 2.25 and 2.55 Ga. Hence, there is no evidence for an Archaean component in the charnockite source. For the granulites, two mafic samples have a $T_{\rm DM}$ in excess of 2500 Ma an therefore classify as Archaean. The model ages of the mafic samples however are characterised by large errors because their ¹⁴⁷Sm/¹⁴⁴Nd is highly similar to the depleted mantle model. Hence, the intersection between the two curves is at a low angle leading to a large uncertainty on the model age. These Archaean mantle depletion ages should therefore be regarded with caution; the more felsic granulites provide less ambiguous $T_{\rm DM}$ ages. The neodymium model ages of the granulites are in overall accordance with the timing of the major crust forming event during the Transamazonian orogeny *(see section 2.3).*

The metadolerite and metagabbro were considered in the field to have a potentially comagmatic origin with the charnockite suite. It was argued that these lithologies represent a juvenile mafic melt that mingled and interacted with the charnockitic magma *(see section 4.3)*. As zircon dating of the charnockites has indicated a crystallisation age of around 1975 Ma, a similar mantle depletion would be expected for the two gabbroic rocks. No such evidence is found: both have $T_{\rm DM}$ ages in excess of 2.3 Ga. As explained above, model age calculation for mafic samples is often troublesome and associated with large uncertainties. On this basis, it is impossible to unequivocally state whether the gabbroic rocks are contemporaneous with the charnockite magmatism or if they find their origin earlier in the history of the Guiana shield.

5.4 – Feldspar thermometry

Two samples were analysed for ternary feldspar thermometry with the electron microprobe *(see section 3.5)*. Sample MKS 22 was taken at the summit of Misty Mountain and is one of the five samples selected for zircon dating and trace element study. This provides an excellent opportunity to compare crystallisation temperatures determined by two hugely contrasting methods: Ti-in-zircon and ternary



feldspar thermometry. The second sample, MKS 30, is derived from the waterfall on the northern flank of Misty Mountain.

In grains with coarse exsolution *(see figure 5.19a)*, the alkali-feldspar and plagioclase zones were analyzed individually with spot analysis and subsequently integrated to a single, ternary feldspar composition using image analysis. Three mesoperthite grains characterised by fine, lamellar exsolution *(see figure 5.19b)* were analyzed by raster- and/or map analysis yielding average ternary compositions directly.

Strontium is present in both alkali-feldspar and plagioclase at a very constant level of 0.23-0.27 wt% SrO. In the raster analyses, strontium is somewhat higher: 0.36-0.38 wt%. These concentrations result in a strontium content of \sim 0.006 Sr-atoms per formula unit (pfu). This concentration is unlikely to affect the calculated temperatures.

Figure 5.19 – Backscatter electron (BSE) images of: **a**) grain MKS 30-4, an antiperthite with blocky patches of alkali-feldspar (light grey) exsolving from a plagioclase host. The coarse exsolution in this grain allowed analysis using a 10µm spot; **b**) mesoperthite MKS 22-3 with very fine lamellae of alkali-feldspar and plagioclase. This grain was analysed with both map- and rasteranalysis; The darkest grey mineral in the upper left corner of both images is quartz. Barium is completely absent from plagioclase, but is present in small amounts (1.0-1.2 wt% BaO) in alkali-feldspar, which forms a solid solution with barium feldspar (celsian, $BaAl_2Si_2O_8$). In the integrated ternary feldspar compositions, the concentration of barium is significantly diluted by the Ba-free plagioclase leading to a celsian component of less than 0.008 pfu. This minor barium contribution is regarded to be negligible.

Alkali-feldspar in selected grains in sample MKS 22 and 30 has a homogeneous composition of $An_{0.07}$. $_{0.20}Ab_{6.7-10.6}Or_{89,3.93,2}$ with MKS 22 plotting slightly more towards albitic compositions *(see figure 5.20)*. On the other hand, the plagioclase composition for the two samples is significantly different. The plagioclase in MKS 22 has a larger albite component than MKS 30: $An_{18.9-19.0}Ab_{80.2-80.4}Or_{0.67-0.77}$ and $An_{22.7-23.3}Ab_{75.5-75.9}Or_{0.93-1.4}$ respectively *(see figure 5.21)*.

Image analysis also revealed a large difference between the two samples. In MKS 22, alkali feldspar constitutes 43-46% of the feldspar grains, which is in sharp contrast with the 17-25% alkali-feldspar in MKS 30. Obviously, the integrated ternary feldspar compositions for both samples are also dissimilar. MKS 22 yields ternary feldspar compositions that are truly mesoperthitic: $An_{10,3-11,1}Ab_{48,4-50,6}Or_{38,3-41,4}$. The map- and raster analyses of fine lamellar exsolution in this sample plot close to these compositions but show more scatter. Raster analyses of two grains were duplicated with a map analysis, which is assumed to be more accurate *(see section 3.5)*. The results for the two different methods are outside error were ternary composition is concerned, but agree quite well for the resulting temperatures *(see figure 5.20)*. Map analysis of grain MKS 22-4 gives a composition that is indistinguishable from the integrated composition of spot analyses of grains MKS 22-1 and 22-2. The integrated ternary feldspars for sample MKS 30 have a more plagioclase-rich composition compared to MKS 22. Three grains (MKS 30-2, 30-3 and 30-4) plot very close together but grain MKS 30-1 contains more plagioclase. The range in ternary feldspar composition is $An_{17.4+19.5}Ab_{58.6-65.0}Or_{15.6-24.1}$.



Figure 5.20 – Alkali-feldspar, plagioclase (open symbols) and integrated ternary feldspar (closed symbols, determined by image analysis) compositions for spot-analysed grains in samples MKS 22 and 30.

Ternary feldspar compositions were solved graphically to yield temperatures using the model by Fuhrman and Lindsley (1988). Generally, crystallisation temperatures between 940 and 990 °C are obtained. Spotanalysed temperatures for sample MKS 22 are the highest in the data set at 987 and 988 °C. Map analyses of grains MKS 22-3 and 22-4 yield 942 and 978 °C respectively. Raster analysis of the same grains are within 20 °C of the map analysis temperatures, despite the markedly different composition *(see above)*. The single grain analysed only with raster analysis (MKS 22-5) yields a temperature of 958 °C. Four grains in sample MKS 30 were determined by spot analysis only. Three of them cluster between 954 and 970 °C, while the compositional outlier (MKS 30-1) records a much lower temperature of 889 °C. To summarize: antiperthitic and mesoperthitic feldspar from the two samples clearly indicate high crystallisation temperatures at or just exceeding 950 °C. The reproducibility of these temperatures with only one obvious outlier provides confidence that ternary feldspar thermometry records magmatic temperatures and is not significantly affected by later stage re-equilibration.



Figure 5.21 – Ternary feldspar temperatures. Isotherms (in °C) calculated with SOLVCALC 2.0 using the model by Fuhrman and Lindsley (1988) at a pressure of 8.5 kbar. **a)** MKS 22, spot analyses; **b)** MKS 22, raster and map analyses. Open symbols are raster analyses, closed symbols are map analyses. Squares: grain 3, diamonds: grain 4, triangle: grain 5 (raster only); **c)** MKS 30, spot analyses

Chapter 6 – Zircon trace elements and geochronology

6.1 – Rationale

An important part of this study is to establish a precise crystallisation age for the magmatic charnockites. The timing of magmatism is crucial in relating partial melting to the ultrahigh-temperature metamorphic event. Highly accurate dating is required since the aim is being able to resolve between the 2070-2050 Ma UHT-metamorphism and the <1990 Ma magmatic pulse. Hence, an accuracy of better than 1% and preferably better than 0.5% is desirable. Whole-rock isotopic dating using for instance the Sm-Nd or Rb-Sr decay systems is not likely to deliver the required accuracy. Even when using isotope dilution to determine parent-daughter ratios, whole-rock dating suffers from problems such as heterogeneous initial ratios and potential open system behaviour leading to errors generally greater than 2%.

Zircon uranium-lead dating has multiple advantages over whole-rock isotopic dating. Uranium has two radioactive isotopes that both decay to an isotope of lead by α-decay. The two decay-systems have largely different half-lives: ²³⁸U decays to ²⁰⁶Pb with a half-live of 4.47 Gyr, similar to the age of the Earth, while the decay of ²³⁵U to ²⁰⁷Pb has a much shorter half-live of 704 Myr (*Jaffey et. al., 1971*). This coupling of two separate but similar decay systems offers large benefits. It allows ages to be calculated on a group of samples with only the analysis of lead isotope ratios without the necessity of determining U-Pb ratios. A synchronous group of samples will define a straight line in a ²⁰⁷Pb/²⁰⁴Pb vs. ²⁰⁶Pb/²⁰⁴Pb diagram with a slope only dependant upon time. This does require a group of samples with identical age and initial lead isotope composition, which can be difficult to ascertain. When a sample has remained a closed system for both U and Pb, the parent-daughter ratios of the two decay systems will evolve along a fixed curve in ²³⁵U/²⁰⁷Pb* and ²³⁸U/²⁰⁶Pb* (the asterisk denotes the radiogenic component of lead, excluding potential common Pb) space called the concordia. The position of a sample on the concordia curve is only a function of time. This implies that a single sample, for instance one zircon crystal, can be dated rather than a group of samples. The requirement of closed system behaviour is rarely met in whole rock samples due to the mobility of uranium (Dickin, 2005). In zircon however, uranium is stable and abundant in the crystal lattice.

Lead on the other hand is strongly excluded from the zircon lattice and the majority of Pb present in the zircon is the product of radioactive decay of uranium. Any lead that was already present in the zircon at the time of crystallisation is referred to as common lead. Since the concordia curve is based on the radiogenic lead component alone, subtracting the common lead is a prerequisite. By measuring the concentration of non-radiogenic ²⁰⁴Pb, it is possible to correct for the contribution of common lead to the radiogenic isotopes. The isotope ratios ²⁰⁷Pb/²⁰⁴Pb and ²⁰⁶Pb/²⁰⁴Pb of common lead can be estimated by using whole-rock Pb isotope composition, a lead evolution model *(Stacey and Kramers, 1975)* or using the Pb isotope composition of a comagmatic phase with a very high Pb/U ratio such as alkali-feldspar *(Ludwig and Silver, 1977; Mezger et. al., 1989; Schoene and Bowring, 2006).*

As mentioned above, lead is not a favourable constituent of zircon and most radiogenic lead resides in weakly bound lattice sites that are often damaged by the α -decay. As a result, lead can potentially be lost from a zircon during a metamorphic episode. For any other decay system, loss of the daughter isotope resets the "clock" and the original crystallisation age can no longer be determined. Due to the two decay branches, the U-Pb system can cope with lead loss and still yield a reliable age. When lead is lost from the sample, the ²³⁵U/²⁰⁷Pb and ²³⁸U/²⁰⁶Pb ratios will shift towards the origin of the concordia curve in a linear way. For a group of samples with the same crystallisation age that experienced various amounts of lead loss during a single event, the ²³⁵U/²⁰⁷Pb and ²³⁸U/²⁰⁶Pb ratios will lie on a straight line called the discordia. The upper intersect of the discordia with the concordia represents the crystallisation age, the lower intercept the age of the lead loss (*Dickin, 2005*).

Zircon ($ZrSiO_4$) is an ideal candidate for U-Pb dating. First of all, it is highly resistant to both mechanical and chemical weathering and has a high closure temperature for uranium. This means that zircon can survive even high grade metamorphic events without the U-Pb system being reset; although lead loss may occur leading to discordant ages. Secondly, zircon is the prime zirconium-bearing phase and is present in almost all igneous rock types and, due to the incompatible nature of Zr, especially abundant in felsic rocks. Most importantly, it concentrates uranium but strongly excludes lead. Common or initial lead may be present, but only in small quantities and it can easily be corrected for without introducing large errors. As a bonus, zircon also incorporates thorium (although less than uranium), allowing a third decay system to be used for geochronology: α -decay of ²³²Th to ²⁰⁸Pb with a half-live of 14.01 Gyr (*Jaffey et. al., 1971*).

In situ analysis of zircon by laser-ablation ICP-MS or ion-microprobe (SHRIMP) allows for direct measurement of the U/Pb ratios required for the construction of a concordia plot. Separate determination of parent and daughter isotope concentrations is not needed, thereby eliminating an important source of error in radiometric dating. Therefore, these in situ techniques offer unparalleled accuracy in U-Pb dating of zircons.

An additional advantage of zircon is that, besides including uranium and thorium in its structure, it also incorporates large amounts of hafnium and heavy rare earth elements (*Rollinson, 1993*). Zircon forms a solid solution with the mineral hafnon (HfSiO₄) and on average contains 1-3 wt% HfO₂. This opens possibilities for in-situ study of hafnium isotope composition of zircon to obtain information on mantle-extraction ages and crustal evolution (*Kemp et. al., 2007*), while rare earth element data can be used to model magmatic processes (*Hanchar and Van Westrenen, 2007*). Coupled with high precision U-Pb dating, zircon forms one of the most powerful tools for constraining magmatic processes.

In this research project, U-Pb dating of the charnockite suite is the primary objective of the in situ zircon study. Five samples from four different localities were selected in the field to provide zircon separates. Additionally, a selection of zircons selected for U-Pb laser-ablation measurements is analysed for trace element composition. Trace element characteristics can be very useful in distinguishing groups of zircons with (slightly) different crystallisation ages. Therefore, the trace element data are presented before the uranium-lead results. Moreover, the analysis of titanium concentration in zircon can be used for the Ti-in-zircon thermometer to determine zircon crystallisation temperatures.

6.2 – Zircon morphology

Cathode luminescence (CL) imaging was used to characterise the internal structure of the selected zircon grains. Emphasis was placed on identifying potential inherited cores that could yield erroneously old ages, but CL imaging also made it possible to recognize inclusions of e.g. apatite. Characteristic zircon morphologies, CL textures and zoning patterns are displayed in figures 6.1 and 6.2.

The zircons from the Bakhuis charnockites selected for in situ analysis are predominantly euhedral, 50-400 μ m long, transparent pale yellow crystals. Inferior grains were less transparent and had a more pronounced yellow to orange-brown colour. The "cloudy" appearance is most likely caused by radiation damage due to α -decay and these zircons are referred to as metamict. The majority of the zircon grains had a length to width ratio of 3:1 to 6:1. More equigranular grains were also present, but elongated to acicular zircons were rare. The habit of the euhedral zircons is rectangular with well developed pyramid-shaped tips *(see figure 6.1c)*, but far more often the pyramid tips are rounded and sub- to anhedral. Multiple grains showed evidence of very recent fracture, most likely experienced during sample crushing. In general, sample MKS 36 yielded the most flawless zircons with numerous crack-free, transparent and euhedral grains.

Cathode luminescence images of the zircons are characterised by light to dark blue colours of variable brightness. Medium blue is most common, although textureless, dark blue grains also occur *(see figure 6.1a, d)*. Very bright zircons often have a striped CL pattern parallel to the longest dimension of the grain *(see figure 6.1a, b and 6.2b)*. Zircons from sample MKS 36 are on average brighter than other samples and the blue colour is transitional to blue-green. Approximately one third of the zircons from sample MKS 26 is characterised by the presence of a dark blue veneer around the tips of the grains *(see figure 6.1b)*. This could be caused because the tips of the grains are not exposed at the surface of the grain mount, but this phenomenon is restricted to sample MKS 26. There is no obvious correlation between crystal morphology and CL colour or brightness.

Zoning is a common feature of zircons and is caused by the heterogeneous distribution of trace elements *(Hoskin and Schaltegger, 2003)*. Oscillatory and sector zoning patterns are deemed typical of magmatic zircon and both are present in the Bakhuis zircons. In particular zircons from sample MKS 36 often display textbook examples of magmatic zoning *(see figure 6.1d, 6.2c, f)*. Oscillatory zoning is the





Figure 6.1 – transmitted light and cathode luminescence photographs of representative zircons. **a**) sample MKS 22 with i.a. a very bright CL grain, a dark blue zoned grain and a large grain with a complex zoning pattern with a dark core overgrown by a brighter rim; **b**) sample MKS 26 with good examples of the dark blue veneer in some grains, especially the grain top-right. Also note the sector zoning in one grain; **c**) sample MKS 36 with examples of euhedral, flawless zircons. Despite its euhedral habit, the grain in the top-right exhibits a complex CL pattern with a potential inherited core. Also note the two large grains on the left that both have complex CL textures, the upper grain has a dark, euhedral core (note the acicular apatite inclusion in transmitted light) while the lower grain displays multiple stages of resorption; **d**) sample MKS 36 with excellent examples of magmatic zoning in zircon. Several grains have a more complex, sector zoned core that is overgrown by a oscillatory zoned rim. Evidence for resorption however is lacking and these textures are interpret as magmatic. Note the elongated zircon in the top-left corner with a dark, featureless CL pattern and a yellow apatite inclusion in the centre.















Figure 6.2 – transmitted light and cathode luminescence photographs of representative zircon grains. a) sample MKS 26 with the only zircon grain with an obvious anhedral inherited core which is especially well visible in transmitted light; b) sample MKS 19 with a very bright grain with a striped CL pattern; c) textbook example of oscillatory magmatic zoning in a zircon from sample MKS 36. Note the apatite inclusions only visible in transmitted light; d) sample MKS 36: a grain showing a dark blue, featureless CL pattern that contains multiple inclusions (probably apatite); e) large zircon from sample MKS 36 that contains four acicular apatite inclusions. Note that the inclusions are not visible in the CL image; f) blue-green CL colours in sample MKS 36 and excellent examples of magmatic sector zoning in zircon; g) two inclusions in zircons from sample MKS 38. The yellow inclusion on the right is probably apatite, the pink inclusion in the grain on the left is unidentified.

most frequently occurring zoning pattern, but sector zoning is also common and often present in the core of zircon grains. Evidence for punctuated growth of the zircon grains is provided by the presence of internal resorption boundaries in many grains *(see figure 6.1a-d)*. Resorption boundaries do not necessarily imply an inherited core but can be formed during a single magmatic growth phase of zircon *(Hoskin and Schaltegger, 2003)*. Nonetheless, grains with very complex zoning patterns were usually not selected for laser-ablation analysis if it was not possible to analyse a single coherent zone. Only one obvious inherited core in the Bakhuis zircons is found in sample MKS 26 (see figure 6.2a).

Inclusions are a common feature in the zircon population. The majority of the inclusions are formed by crystals with a bright yellow-green colour in cathode luminescence images (see figure 6.1d and 6.2d, g) that are probably apatite crystals. They occur as short, stubby anhedral grains, but euhedral acicular crystals are also common (see figure 6.2e). The apatite inclusions are not always visible in CL images when they are not exposed at the surface, but are obvious in the transmitted light photographs and could therefore easily be avoided during analysis. Very rare in the zircon population are pink-coloured inclusions that remain unidentified (see figure 6.2g).

6.3 Trace element characteristics

6.3.1 Rare-earth element variation

Although trivalent rare-earth elements (REE) and yttrium are generally not compatible in the zircon crystal lattice, coupled substitution with pentavalent ions such as Nb⁵⁺, Ta⁵⁺ but predominantly P⁵⁺ allows charge balance to be maintained. Other possible substitutions mechanisms include the incorporation of interstitial Li⁺ and protonation of oxygen (*Hoskin and Schaltegger, 2003*). Due to the lanthanide-contraction, the ionic radii of the heavy REE (HREE) are more similar to the zirconium radius and therefore more readily substitute into the zircon lattice. For instance, the ionic radius of Zr in eightfold coordination (0.084 nm) more closely resembles that of lutetium (0.0977 nm) than the 0.116nm radius of lanthanum (*Shannon, 1976*). This increase in compatibility from the light to the heavy REE gives rise to zircon's characteristic REE-pattern (see figure 6.3). Chondrite normalised (*McDonough and Sun, 1995*) concentrations of the REE vary by more than four orders of magnitude and display a smooth increase from less than 0.01 (La) to over 1,000 (Lu) times chondrite.

Two marked exceptions are the anomalous behaviour of cerium and europium. Cerium can, under oxidising conditions, become tetravalent with an ionic radius of 0.097 nm (Shannon, 1976), which closely resembles the radius of lutetium. Hence, tetravalent Ce⁴⁺ will be preferentially incorporated in the zircon lattice and be more concentrated than expected from the lanthanide-contraction (Hinton and Upton, 1991). The magnitude of this positive cerium-anomaly (Ce/Ce*; see figure 6.4) is directly controlled by the oxygen fugacity and can therefore be used to estimate the fO_2 of the melt. Europium on the other hand can occur in both a divalent and trivalent oxidation state. Due to its large ionic radius (0.125 nm; Shannon, 1976), Eu²⁺ is strongly excluded from the zircon structure and therefore relatively depleted leading to a negative Eu-anomaly. At first glance, it appears impossible that oxidised Ce⁴⁺ and reduced Eu²⁺ could occur simultaneously under the same fO_2 conditions and that zircons can exhibit both a positive cerium- and negative europium-anomaly. Although there is no consensus on this issue, it appears that Eu²⁺ and Ce⁴⁺ can co-exist under certain conditions (Hoskin and Schaltegger, 2003). Moreover, since divalent europium is very effectively incorporated into plagioclase feldspar, this apparent paradox can be explained by plagioclase fractionation, which depletes the melt in europium. Hence, oxygen fugacity may not be the only factor controlling the magnitude of the Eu-anomaly.

Zircons from the Bakhuis charnockites have REE-patterns that are typical of zircon *(see figure 6.3)*. REEconcentrations steeply increase from lanthanum to lutetium and large positive Ce-anomalies and moderate to large negative Eu-anomalies are present. Especially in the middle- and light REE, variation within samples can exceed one order of magnitude. For samples MKS 26 and 36, the rare-earth patterns appear to form two distinct groups, while other samples show a more continuous increase from higher to

Figure 6.3 (next two pages) – extended rare-earth element diagrams normalised to CI chondrite (McDonough and Sun, 1995). Note the overall limited intra- and inter-sample variation in rare-earth element patterns and concentrations.





lower REE-concentrations. The variable REE-concentrations are probably caused by igneous fractionation. This suggests that zircon is an early fractionating phase and has a major influence on the REE budget of the rocks. Notable is that the grain with an anhedral core in sample MKS 29 *(see figures 6.2a and 6.3)* does not have a different REE-pattern or concentration although it does plot to the high side. There is no significant difference between the five samples where REE-concentrations or patterns are concerned.

Trace element analyses of zircons can be hindered by the presence of microscopic inclusions of apatite (e.g. *Fulmer and Kruijer, 2009*). Apatite has a REE-pattern exactly opposite to zircon with light REE enrichment. Incorporation of these inclusions can lead to anomalously high concentrations and increased scatter of the LREE (La to Nd) with lanthanum concentrations in excess of 100 times chondrite. The current Bakhuis dataset appears not to be affected by apatite contamination. There is marginal scatter in the LREE but concentrations are consistently less than chondrite. The variation is more likely caused by lanthanum concentrations that are approaching the detection limit rather than significant contamination by apatite inclusions.

6.3.2 Other trace element variation

Trace element variation in zircon is ideally expressed as a function of amount of zircon fractionation and hence melt evolution. As mentioned in section 6.1, zircon ($ZrSiO_4$) forms a solid solution with hafnon ($HfSiO_4$) where zircon occupies the high-temperature end. This implies that early fractionating zircon has a lower Hf/Zr-ratio than late crystallising grains and that the Hf-content of zircon can be used as a proxy for melt evolution (*Linnen and Keppler, 2002; Lowery Claiborne et. al., 2006*). Therefore, trace element variation is plotted against hafnium concentration in figure 6.4.

Hafnium displays a convincing positive correlation with U/Th ratios. The uranium/thorium ratio therefore appears to be governed by melt evolution and can also be used as a proxy for the amount of zircon fractionation. Zircons from sample MKS 38 however, plot slightly off the main correlation trend towards higher U/Th ratios. Uranium concentrations lie between 40 and 300 ppm U, which is on the low side compared to average zircons (Hoskin and Schaltegger, 2003). There is a clear positive correlation between Hf and U-concentrations indicating that zircon fractionation does not readily deplete the melt in uranium. The opposite is true for the rare-earth elements (expressed as the sum of all REE) that decrease with increasing Hf-content and U/Th-ratios. This could imply that zircon is the predominant phase controlling the REE-budget or that another REE-rich phase (e.g. apatite) is fractionating simultaneously. The steepness of the rare-earth element patterns is not easily connected to melt evolution. The HREE slope (Lu/Tb_N) is constant with Hf-content but the MREE slope (Gd/Pr_N) does exhibit a mild correlation with hafnium for samples MKS 22, 26 and 36. In samples MKS 19 and 38 however, the Hf-Gd/Pr_N correlation is non-existent. A similar relationship exists between Hf-content and Ce-anomaly: a mild correlation for samples MKS 22, 26 and 36 but none for MKS 19 and 38. A very good negative correlation is present between Eu/Eu* and hafnium concentration. This probably implies that the magnitude of the Eu-anomaly is not primarily controlled by the $f O_2$ of the melt, but that plagioclase fractionation is of more influence. Since divalent europium is preferentially incorporated, fractional crystallisation of plagioclase feldspar will deplete the co-existing melt in europium relative to the other REE. Zircon crystallising in that melt will inherited the Eu-depleted signature. The magnitude of the Euanomaly should increase (i.e. Eu/Eu* decreases) with increasing plagioclase fractionation and melt evolution. The good correlation between melt evolution (as recorded by the Hf-content) and Eu-anomaly provides solid evidence that plagioclase fractionation exerts the major control on the europium-anomaly in zircon. Finally, yttrium concentrations in the zircons display an excellent positive correlation with total REE-content (not plotted). This is easily explained since trivalent Y behaves similar to heavy rare-earth elements such as holmium (see figure 6.3).

Figure 6.4 (next page) – trace element variation diagrams for the Bakhuis zircon samples. The colour-coding is identical to figure 6.3. Green plusses: MKS 19; Dark-blue circles: MKS 22; orange triangles: MKS 26; Light-blue diamonds: MKS 36; Purple X-es: MKS 38. Σ REE represents total rare-earth elements (La-Lu) concentrations, the subscript "N" denotes CI-chondrite normalised (McDonough and Sun, 1995) ratios. Note that Ce/Ce* and Eu/Eu* are plotted on a log-scale. Cerium- and europium-anomalies are calculated as the geometric mean of the normalised concentrations: e.g. Ce/Ce* = Ce_N / $\sqrt{(La_N \times Pr_N)}$



Similar to the rare-earth data, the other trace elements do not allow the distinction of different groups of samples. Only sample MKS 38 tends to plot away from the trends generated by the other samples in U/Th and Σ REE versus hafnium plots. The presumed inherited core in sample MKS 26 (see figure 6.2a) can not be distinguished based on trace element data. Samples MKS 36 and 38 have a whole rock SiO₂ content of less than 60 wt% and represent the most mafic endmembers of the charnockite suite. MKS 36 in particular has a cumulate texture enriched in plagioclase and zircon. Zircons from these samples also tend to have the lowest Hf-content, confirming the early crystallisation of these samples.

6.3.3 Ti-in-zircon thermometry

Small amounts of titanium can substitute for silicon in zircon (Watson et. al., 2006). Since this Ti-Si substitution has shown to have a predictable temperature dependence, it has been calibrated as a geothermometer by Ferry and Watson (2007). The diffusion of titanium in zircon is only slightly faster than diffusion of U, Th and Hf and therefore the titanium-in-zircon thermometer has the potential to retain the signature of magmatic crystallisation conditions (Cherniak and Watson, 2007). The thermometer calibrated by Ferry and Watson (2007) is dependent on the activities of SiO₂ and TiO₂ in the melt and gives the following relationship between Ti-concentration in zircon and temperature:

$$T_{Ti-in-zrc}[K] = \frac{-4800}{\log(Ti_{zrc}[ppm]) - 5.711 + \log(a_{SiO_2}) - \log(a_{TiO_2})}$$

For silica-saturated felsic rocks containing abundant quartz, the SiO₂-activity can safely be assumed to be at unity, which is the case for sample MKS 19, 22 and 26. Samples MKS 36 and 38 on the other hand are barely silica saturated and hence the SiO₂-activity might be less than 1. It must be noted that especially sample MKS 36 has a cumulate texture with respect to plagioclase and zircon and therefore the chemistry of this sample could be different from the melt from which zircon crystallised. As can be seen in figure 6.5, decreasing the SiO₂-activities from 1 to 0.5 will only change the Ti-in-zircon temperatures for by ~70 °C. It is difficult to imagine that the silica-activity of a felsic crustal melt would be less than 0.8 and therefore the uncertainty on the SiO₂-activity is not of that much influence on the resulting temperatures. Titanium-activities are more difficult to estimate. Based on the high whole-rock titanium concentrations, it was assumed that a significant part of the opaque minerals in the Bakhuis charnockites consists of ilmenite or another Fe-Ti-oxide phase. Their ubiquitous presence suggests a high titanium-activity, probably between 0.7 and 1. In line with other granitoid studies *(*e.g. *Fulmer and Kruijer, 2009)*, a Tiactivity of 0.7 was adopted in all temperature calculations.



Figure 6.5 – effect of variable TiO_2 and SiO_2 activities on the Ti-in-zircon thermometer calibrated by Ferry and Watson (2007). For TiO_2 and SiO_2 activities at unity, a zircon containing 25 ppm Ti will yield a temperature of 840 °C.



Figure 6.6 – Ti-in-zircon crystallisation temperatures for the Bakhuis zircon samples calculated according to the thermometer by Ferry and Watson (2007). A SiO₂-activity of 1 and TiO₂-activity of 0.7 have been used. Probability density plots were constructed with Isoplot 3.71 (Ludwig, 2008) using propagated uncertainties for the Ti-concentrations and calibration errors reported in Ferry and Watson (2007). Dashed lines indicate whole-rock zircon saturation temperatures according to Watson and Harrison (1983)

Zircons from the Bakhuis charnockites typically contain between 5 and 30 ppm titanium *(see appendix 3.1).* Using the Ti-in-zircon geothermometer *(Ferry and Watson, 2007)*, these concentrations are equivalent to crystallisation temperatures between 700 and 950 °C *(see figure 6.6).* The individual samples show a weak bimodal distribution in Ti-in-zrc temperatures with peaks at 750-775 °C and 850-875 °C. When all samples are combined, the bimodal distribution is better developed. This suggests that there are two distinct populations of zircon formed during an early and a late crystallisation phase. What is surprising however, is that the peak in the Ti-in-zrc temperature distributions consistently plot well below whole rock Zr-saturation temperatures *(Watson and Harrison, 1983).* This is in sharp contrast with other studies *(Harrison and Watson, 1983; Harrison et. al., 2007)* that indicate that the onset of zircon crystallisation lies at temperatures 50-100 °C above whole rock Zr-saturation temperatures.

A critical evaluation of Ti-in-zircon thermometry and comparison with other estimates of crystallisation temperatures (e.g. ternary feldspar thermometry) with their respective merits and weaknesses will be provided in section 7.3.

The relationship between various trace elements in zircon and their crystallisation temperatures derived from the Ti-in-zircon thermometer are displayed in figure 6.7. Important to note is the good correlation between hafnium-concentration and $T_{\text{Ti-in-zrc}}$, that indicates that hot, early crystallised zircons contain less Hf than zircons that have fractionated at lower temperatures. This is in good agreement with the zirconhafnon thermodynamics described in section 6.3.2. An obvious implication is that the same correlations must exist between the selected trace elements with $T_{\text{Ti-in-zrc}}$ as with Hf-contents as depicted in figure 6.4. As is evident from figure 6.7, this is indeed the case. The excellent correlation between Eu/Eu* and $T_{\text{Ti-in-zrc}}$ suggest that "cold" zircons have crystallised from a melt that already experienced significant plagioclase fractionating imparting a relatively Eu-depleted signature on the zircons.

One grain from sample MKS 22 (dark blue circles) forms an obvious outlier in e.g. U/Th, Hf and Eu/Eu* plots. This grain does not display anomalous behaviour in the trace element variations plots in figure 6.4. Its deviation in the $T_{Ti-in-zrc}$ plots is therefore probably caused by analytical error in the titanium-measurement.

6.4 U-Pb geochronology

Before venturing into a presentation of the geochronological results obtained by laser-ablation analysis of zircon, I will first address the issue of the errors on the U-Pb decay constant. The original uranium decay constants were determined by α -counting experiments on high-purity ²³⁸U and ²³⁵U metals by Jaffey et. al. (1971) and found to be $1.55125 \times 10^{-10} \pm 0.108\%$ and $9.8485 \times 10^{-10} \pm 0.137\%$. These authors do however report an unknown source of drift in the ²³⁵U-measurements so that two consecutive experiments did not agree within error. It has therefore been recommended that the errors reported by Jaffey et. al. (1971) should be doubled for geochronological purposes (Mattinson, 1987). With the increase in analytical precision, consistent discrepancies in U-Pb ages have been noted, suggestive of a systematic inaccuracy in one of the uranium decay constants (Mattinson, 2000; Begemann et. al., 2001; Schoene et. al., 2006). Based on the observations of Jaffey et. al. (1971), the uranium-235 decay constant is the most likely candidate to be slightly off. Therefore, a renewed decay constant for ²³⁵U of 9.857×10⁻ ¹⁰ has been proposed (Mattinson, 2000). This value is in excellent agreement with the study by Schoene et. al. (2006). Nevertheless, the new data have not resulted in a major change in the geochronological community and the decay constants by Jaffey et. al. (1971) are still solely used. To allow comparison with other U-Pb or Pb-Pb ages, I have decided to adopt the decay constants and associated errors of Jaffey et. al. (1971). Errors on calculated U-Pb ages take into account these uncertainties.

The results of the zircon U-Pb dating are displayed in figure 6.8. For every sample, four different graphs are shown. The upper graph depicts all laser-ablation analyses per sample after data reduction using Iolite plotted in a concordia diagram. As already mentioned in section 3.4.3, some analyses were excluded for various reasons. For instance, very short analyses or analyses close to or on top of inclusions were not incorporated in the age calculations. These excluded analyses are displayed in the upper graph together with the analyses that were included. Error bars have been omitted in these graphs for the sake of clarity;

Figure 6.7 (next page) – variation diagrams of various trace elements versus Ti-in-zircon temperatures. Symbols and colours are the same as figure 6.4.



the aim is to highlight that the excluded analyses have no major influence on the dataset. In the middle graphs, probability density plots of lead-lead ages have been plotted. The left plots includes all samples, the right plot only the selected analyses. The easiest way to derive age information from U-Pb data, is a ²⁰⁷Pb/²⁰⁶Pb age. By neglecting the uranium component, any elemental fractionation effects *(see section 3.4.3)* are eliminated. On the other hand, Pb-Pb ages do assume concordance of the sample. For discordant samples, the ages will be underestimated. Moreover, correction for common lead is critical for Pb-Pb ages. As already mentioned, common lead is not an issue in this study. The advantage of probability density plots of Pb-Pb ages is that they allow the possibility to distinguish between zircon populations with different ages. Using the ²⁰⁷Pb/²⁰⁶Pb ratios obtained with Iolite, ages were calculated according to the formula:

$$\frac{{}^{207}Pb}{{}^{206}Pb} = \frac{1}{137.88} \frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1}$$

In this formula, 1 / 137.88 represents the present-day ²³⁵U/²³⁸U ratio that can considered to be constant in nature. Probability density plots generated using Isoplot 3.71 *(Ludwig, 2008)* take into account the errors on the ²⁰⁷Pb/²⁰⁶Pb ratios as determined by Iolite. Since these errors are on average between 0.5 and 2%, the apparent bimodal distributions in the histograms present for some samples are not witnessed in the probability density curves. Due to these large errors, it is impossible to unambiguously distinguish between different zircon populations for any of the samples. Therefore, all selected analyses per sample have been taken together in a single group for the final U-Pb age calculation.

The lowest graph displays conventional ²⁰⁶Pb/²³⁸U versus ²⁰⁷Pb/²³⁵U concordia diagrams (Wetherill, 1956) with the U-Pb ages of the samples as calculated using Iolite normalised data and Isoplot 3.71 (Ludwig, 2008). Decay constant errors are incorporated in the concordia curve. Several issues arise from these graphs that will be addressed before the resulting ages are discussed. First, the errors of individual analyses are large compared to other U-Pb studies. This probably finds it origin in the relatively small laser spot size used (mostly 30µm) for the analyses. Per sample, practically all measurements are within error. These large errors preclude the resolution to distinguish between multiple generations of zircons formed within a short time period, i.e. early and late crystallising zircons as suggested by the trace element data. Nonetheless, the large error do not preclude the calculation of an accurate age for the total zircon population per sample. The individual analyses are scattered around the concordia and both weakly normal discordant and weakly reverse discordant analyses are present. For sample MKS 19, more than half of the analyses plots above the concordia. Reverse discordance means either uranium-loss or lead-gain, both of which are geologically hard to justify. Due to the enhanced mobility of lead over uranium in zircon, preferential U-loss is very difficult to accomplish. The loss of uranium must almost certainly be accompanied by lead-loss, wherefore is little evidence in this dataset. Coupled U-Pb-loss will disturb the U-Pb system in such a way that a concordia plot can no longer be used to derive age information. The incorporation of lead is also difficult to envisage. Lead contamination is certainly possible during subaerial exposure of the rocks and sample handling, but Pb would be deposited on the grain surface or in cracks. Since cracks were meticulously avoided during analyses and the first few seconds of every measurement were discarded to avoid surface contamination, Pb-contamination appears not to be a plausible explanation. It has been suggested that reverse discordance can be caused by local Pb-gain where lead moves from more U-rich metamict zones to more pristine parts of the grain (Williams et. al., 1984). The ion-microprobe analyses on which these conclusions are based were characterised by a highly unstable ²⁰⁶Pb signal during ablation of a single pit while the uranium signal remained stable. This is not the case for the Bakhuis zircons. Signal intensities did vary throughout a measurement, but in a consistent way: raw U/Pb-ratios were constant. Recently, it has been recognized that reverse discordance is a feature typical of ion probe and laser-ablation analyses. It is very rare phenomenon in conventional methods using TIMS and is therefore more likely caused by elemental fractionation during ablation (Mezger and Krogstad, 1997). A potential source of this uncorrected fractionation lies in matrix differences between samples and the calibration standard. A prerequisite for adequate elemental fractionation correction is identical response to the laser-ablation for standards and samples (see section 3.4.3). Any discrepancies could lead to uncorrected errors. This is also the most probable explanation for the weak reverse discordance of the Bakhuis zircons. In general, all individual analyses are within error of the concordia and evenly distributed below and above. Therefore, it is concluded that errors in elemental fractionation corrections due to sample-standard matrix dissimilarity have caused the reverse discordance rather than Pb-gain.

Probability density plots and error-weighed average thorium-ages are plotted in figure 6.9 using Iolite normalised data according to the formula:

$$t = \frac{\ln(1 + (^{208}Pb/^{232}Th))}{\lambda_{232}}$$

The thorium ages should however, be regarded with caution because of the atypical behaviour of elemental fractionation during analysis *(see section 3.4.3)*. Nevertheless, the average ages are in agreement with the U-Pb ages, but the spread in the Th-Pb ages is much larger. Highly anomalous outliers (<1%) are present with individual analyses as low as 1700 Ma up to 2300 Ma. These extreme outliers have been omitted from figure 6.9 for the sake of clarity.

6.4.1 U-Th-Pb ages of the Bakhuis charnockites

In this section, the results of the radiometric dating of the charnockites will be discussed. As already mentioned in the preceding section, all of the samples are characterised by mild normal and reverse discordance that is most likely caused by standard-sample matrix differences. Whether or not the source of the discordance is natural, it does eliminate the use of Pb-Pb ages to obtain a high precision age. Therefore, all ages are calculated as discordia curves where the upper intersect age is presumed to be the magmatic age. Errors on the lower intercept ages are very large, but all cluster around present-day. This can be explained by recent lead-loss due to weathering, or it can be an analytical artefact originating from the calibration problems mentioned above. For every sample, the mean square of weighted deviates (MSWD) is also reported, which is a statistical quantity used to assess the amount of scatter in a regression. When the scatter can solely be explained by analytical error, the MSWD is near unity. Whenever the MSWD is larger than 1, the inferred analytical errors alone are not sufficient to explain the amount of scatter and other causes, geological, causes are present. It is also possible that analytical errors have been underestimated. In common practice, any regression with a MSWD >2.5 is considered an errorchron. For the Bakhuis charnockites, two reasons can be provided for a high MSWD. As noted above, analytical errors in the dataset are large and can easily be underestimated. Moreover, trace element data suggest at least two generations of zircons belonging to an early and a late crystallisation phase. In the light of the high temperatures of the melt from which the zircons crystallised, slow cooling of the magma and prolonged zircon crystallisation over a period of ~5-10 Myr can be supported geologically. Due to the large errors on individual analyses, it was not possible to resolve these timescales. However, prolonged zircon crystallisation will per definition introduce additional scatter in a U-Pb concordia diagram and cause the data to spread out.

Due to reasons explained above, the U-Pb discordia age is deemed most reliable and therefore adopted as the definitive age of a sample.

MKS 19: Misty Mountain

This sample has the most reverse discordant analyses of all samples. The reverse discordance does not appear to have any adverse effects since the Pb-Pb ages form a narrow peak and also the spread in the uranium-lead data is small (MSWD = 1.3). The U-Pb age for this sample is 1977.9 ± 8.7 Ma, which is good agreement with the Pb-Pb age peak at ~1986 Ma. The Th-Pb age (2028 ± 17 Ma) is slightly older and outside error. Two analyses of cores with very bright cathode luminescence did not fall outside the sample range and are therefore interpreted as contemporaneous rather than inherited.

MKS 22: Misty Mountain

MKS 22 is characterised by a perfect normal distribution of the Pb-Pb ages with the peak at ~1992 Ma. Despite the good distribution, this sample shows significant scatter that is reflected in a high MSWD of 2.6. However, the U-Pb discordia age of 1985.6±8.8 Ma is in excellent accordance with the Pb-Pb age and within error of the Th-Pb age (1967±20 Ma). Similar to MKS 22, this sample included two potential inherited cores that were indistinguishable from the other analyses.

Figure 6.8 (next five pages) – U-Pb geochronological results for the Bakhuis charnockites. See text above for additional explanation. Probability density plots are constructed using Isoplot 3.71 (Ludwig, 2008)













Figure 6.9 – 208Pb/232Th zircon ages for the Bakhuis charnockites. Probability density plots are constructed and weighed averages are calculated using Isoplot 3.71 (Ludwig, 2008)

MKS 26: Krong Soela

Sample MKS 26 contains grains with remarkable dark veneer rims (see section 6.2) and the very obvious anhedral core (see figure 6.2a). Both these features however, fail to be reflected in the age of the grains. As is evident from figure 6.8, the anhedral core plots exactly on the discordia curve that defines the age of the sample. Also the dark veneer analyses could not be distinguished from the rest of the data. This sample displays significant scatter resulting in a MSWD of 2.9. In addition, the Pb-Pb ages form a weakly developed bimodal distribution that is barely visible in the probability density curve. Any attempt to divide the total population of zircons into subgroups proved to be unsuccessful. Therefore, the data were taken together into a single concordia plot yielding a U-Pb age of 1963 ± 12 Ma. The high MSWD together with the larger than average error of 12 Myr however, do indicate that this is not the best constrained of all charnockite ages. The lead-lead age of ~1994 Ma and the Th-Pb age of 2016 ± 13 Ma are within error of each other, but well above the U-Pb age.

MKS 36: Zand Creek

The Zand Creek zircon sample (MKS 36) was considered to be the best sample containing the most flawless zircons. Multiple grains were characterised by excellent examples of magmatic zoning *(see section 6.2)* and were free from inclusions or cracks. Only three grains with potential inherited cores were present, but again none yielded different ages. The Pb-Pb ages for MKS 36 form a broad distribution, which is caused by the above-average discordance for some analyses. Despite the wide peak, the average Pb-Pb age (~1985 Ma) is identical to the U-Pb discordia age of 1984.6 \pm 9.8 Ma. The low MSWD of 1.3 gives confidence in the reliability of this age, and even the Th-Pb system yielded a undistinguishable result: 1994 \pm 12 Ma.

MKS 38: Moi-Moi

Sample MKS 38 yields the youngest age of the five charnockite samples. The U-Pb discordia age is 1959.3 \pm 8.7 Ma, which is younger than the average of the lead-lead ages (~1984 Ma) and the Th-Pb age (2028 \pm 14). The U-Pb analyses show mild scatter resulting in a MSWD of 2.4. Three analysed potential cores provide the same age as the rest of the analyses. Contrary to sample MKS 26 that is also significantly younger than the other three samples, there is no evidence for multiple zircon populations in MKS 38.

6.4.2 Summary

Uranium-lead zircon dating of the Bakhuis charnockites has revealed that the zircons in these rocks crystallised between 1959 and 1986 Ma during the Paleoproterozoic *(see figure 6.10)*. Since these zircons exhibit many features typical of igneous zircon and lack evidence for subsequent recrystallisation, ages derived from these zircons can safely be assumed to represent the age of intrusion of the charnockites. Zircon grains from the samples are weakly discordant and define discordia curves in a conventional ²⁰⁶Pb/²³⁸U versus ²⁰⁷Pb/²³⁵U concordia diagram. The upper intersect of the discordia curves with the concordia is taken to represent the crystallisation age, while the lower intercept age is poorly constrained and not assigned any geological significance.

Samples MKS 19 and 22 taken from Misty Mountain and sample MKS 36 from the Zand Creek are analytically indistinguishable from each other, which is also valid for samples MKS 26 from Krong Soela and MKS 38 from Moi-Moi. These two groups however, differ in age by about 20 Myr. While it can be argued for that the age obtained on MKS 26 is a mixture of two or more zircon populations with different ages and hence unreliable, there are no sound reasons to dismiss the age for sample MKS 38. As will be discussed in detail in section 7.4 and 7.5 however, the two younger samples might not necessarily be representative of the whole charnockite suite. Sample MKS 26 from Krong Soela shows evidence for mixing with a mafic component while MKS 38 is sampled in close proximity to the large metagabbro body at Moi-Moi. Therefore, when quoting an average age for the charnockites, more emphasis is placed on the three older samples. To conclude: an age of 1975 Ma will be used as an average age for e.g. age-correction of radiogenic isotopes *(see section 5.3).*



Figure 6.10 – summary of the zircon uranium-lead discordia ages obtained on the Bakhuis charnockite samples.

Chapter 7 – Discussion

7.1 – The Bakhuis charnockites: a typical C-type magma?

7.1.1 Definition of the C-type magma

A prerequisite for the definition of orthopyroxene-bearing quartzo-feldspathic rocks as charnockites is an undisputedly igneous origin of the rocks in question (Frost and Frost, 2008); orthopyroxene should be a magmatic phase and not originate from metasomatic replacement of hornblende. The most convincing evidence for an igneous origin of the Bakhuis charnockites is provided by the field relationships. The charnockites are very homogeneous on the hand sample and outcrop scale and no indications for compositional banding are present. On a thin section scale, the Bakhuis charnockites are characterised by an igneous texture. Their porphyritic texture with plagioclase phenocrysts and sub- to euhedral pyroxene crystals is typical for magmatic rocks. Compelling evidence is formed by the often strong magmatic zoning in the large plagioclase phenocrysts. Zoning is continuous from a more calcic core to a more sodic rim, commonly with by antiperthitic exsolution in the plagioclase rims. The porphyritic texture is in sharp contrast with the orthopyroxene-bearing quartzo-feldspathic granulites in the Bakhuis belts. These metamorphic rocks, although highly similar to the charnockites in mineralogy, are distinct by their equigranular, recrystallised texture. As Karlsbad twinning in feldspar is a relatively rare feature in metamorphic rocks, its ubiquity in charnockitic plagioclase is also supportive of an igneous origin. Moreover, several charnockite samples appear to be enriched in plagioclase and zircon by crystal accumulation. Large, strongly zoned plagioclase crystals are aligned and enriched in these samples indicating the influence of fractional crystallisation. Based on these observations, it can be concluded that Bakhuis charnockites are truly magmatic in origin.

Charnockites are characterised by a typical petrography and geochemical composition, that led to the recognition of a separate "C-type magma" (*Kilpatrick and Ellis, 1992*). The main geochemical distinguishing features are the much higher TiO₂, P₂O₅, K₂O and Zr concentrations compared to average I-type granites (*Kilpatrick and Ellis, 1992; Young et. al., 1997; Zhao et. al., 1997; Rajesh, 2007*). The high Ti, P and Zr contents are expressed in high modal abundances of ilmenite, apatite and zircon respectively. Although TiO₂ and P₂O₅ concentrations in the Bakhuis samples are not as high as the Antarctic samples from Zhao (1997) for instance, these elements are still enriched compared to typical I-type granite. In contrast, charnockites differ from A-type granites (e.g. *Collins et. al., 1982*) in several aspects as well. Although A-type granites can exhibit the same high field strength element enrichment, they are generally highly silicic while charnockites span a wide range of silica-compositions. The crucial difference is formed by the very magnesium-poor nature of A-type granites, which persistently have whole rock Mg# below 10 and often <5. The C-type magma described by Kilpatrick and Ellis (1992) is characterised by magnesium numbers between 40 and 25, which is also the case for the Bakhuis charnockites (*see figure 5.3*).

Considering the petrography of the Bakhuis suite, the charnockites are also in agreement with the generalisation in Kilpatrick and Ellis (1992). Orthopyroxene is invariably present, a prerequisite for the definition as charnockite. Moreover, charnockites share common petrographic features indicative of increased crystallisation temperatures compared to I-type granites. Hornblende is relatively rare and often biotite is the sole hydrous phase present. Moreover, the common occurrence of ternary feldspar in the form of antiperthite and more rarely mesoperthite, and the rare presence of inverted pigeonite attest to high crystallisation temperatures in the Bakhuis charnockites. Although the Bakhuis samples contain above average hornblende, this appears to be restricted to the most felsic samples. The persistent presence of pyroxenes over hornblende and multiple textural indications of high temperature crystallisation justify the recognition of the Bakhuis charnockites as being similar to the C-type magma defined by Kilpatrick and Ellis (1992).

7.1.2 Charnockite source models

As summarised in the introduction of this thesis, multiple models have been presented in the literature to explain the generation of this typical C-type magma with its high HFSE concentrations and anhydrous nature. The variety in structural and tectonic settings in which charnockites occur *(Newton, 1992)*

suggests that multiple mechanisms could be capable of producing the anhydrous melts. Many of these models however, do not discuss charnockites that are in good agreement with the C-type magma and have marked differences to the general C-type geochemistry. Nevertheless, a selection of highly variable models will be critically evaluated and their feasibility to explain the Bakhuis charnockites will be discussed.

The association of lower crustal charnockites with shallower rapakivi-granites led Hubbard (1989) to the conclusion that charnockites were residues after the extraction of a granitic melt. This model is in sharp contrast with the per definition magmatic origin of charnockites, and is therefore unlikely the case in the Bakhuis belt. Moreover, it is difficult to envisage how a residue after melt extraction can have high concentrations of incompatible elements and the large range in silica-content recorded by the Bakhuis charnockites (55-76 wt% SiO₂). The same argument applies to the cumulate model advocated by for instance Emslie (1991) and Duchesne and Wilmart (1997). Similar to the suggestion by Hubbard (1989), these studies focus on charnockites in anorthosite-mangerite-charnockite-granite (AMCG) suites. The authors provide sound evidence that charnockites can in fact be generated by fractional crystallisation and magma evolution. However, this model is incompatible with the high silica and incompatible element composition of the Bakhuis samples. Moreover, the Bakhuis samples themselves define a melt evolution trend and cumulitic samples are present (see section 7.2).

The residual source model for the generation of A-type granites (Collins et. al., 1982) and charnockitic melts (Sheraton and Black, 1988; Munksgaard et. al., 1992) has suffered severe criticism and is now largely rejected. This model proposed that charnockites (and A-type granites) are the products of second-stage melting of a melt depleted source. Dehydration melting of a fertile, lower crustal source leads to the extraction of a regular hydrous I-type granite, leaving behind a dehydrated, depleted residue. Renewed melting of this depleted residue was deemed to produce either A-type granites or charnockites (Collins et. al., 1982). Creaser et. al. (1991) however, showed that the melt depleted residue is too K-depleted to yield the potassium-rich A-type granites or charnockites upon second-stage melting. An additional argument against the residual source model is provided by Mg-Fe thermodynamics. The Mg# of a melt will always be lower (more ferroan) than that of the residue (Winter, 2001). Extraction of an I-type granite will leave behind a magnesium-rich residue. Re-melting of this residue will therefore result in a melt with a higher Mg# than the previously extracted I-type granite. This is in sharp contrast with the highly ferroan nature of A-type granites. This argument also applies to charnockites in general and the Bakhuis suite in particular, as they have a Mg# that is intermediate between A-type granites and I-type granites.

All the models discussed so far have focussed on a predominantly crustal source for charnockitic magmas. Examples are however, documented where charnockites appear to be the products of prolonged fractional crystallisation of mantle-derived melts that have interacted little with the crust *(Eggins and Hensen, 1987; Sheraton et. al., 1992; Mikhalsky et. al., 2006)*. Fractionation of mafic phases and plagioclase from a basaltic primary magma will deplete the remaining melt in Mg, Fe and Ca and increase the silica-content. Large amounts of fractionation can therefore ultimately result in a final melt fraction that has a felsic, granitic composition. Examples are provided by the occurrence of volumetrically small bodies of felsic rocks at mid-ocean ridges. The charnockites in the studies mentioned above are geochemically similar to these ocean-ridge granites. This model however, is not applicable to the Bakhuis charnockites for multiple reasons. The ubiquity of a subduction zone signature in all samples is not compatible with a predominantly non-subduction related, mantle-derived origin. Moreover, the metadolerites and metagabbro that are proposed to be juvenile melts, are also characterised by a negative Nb-Ta anomaly. It is however, difficult to argue for the prolonged fractional crystallisation model even if the gabbroic samples are considered to represent the primary magma.

As noted above, the Mg# of the solid phase is per definition higher than that of the co-existing melt; i.e. the Mg# of the fractionating phases is higher than that of the remaining melt. Continuous fractionation will significantly deplete the melt in magnesium and the final, granitic melt therefore has a highly ferroan composition (Mg# <10). This is in line with the charnockites from for instance Mikhalsky et. al. (2006), which have very low magnesium numbers. As is evident from figure 5.3, this is not the case for the Bakhuis charnockites. Volumetric considerations offer an even more compelling argument against the prolonged fractional crystallisation model in the case of the Bakhuis charnockites. Shifting the composition of a primary basaltic magma (~45 wt% SiO₂) to a granitic composition (70-75 wt% SiO₂) requires at least 95% fractionation of mafic phases. If this amount of fractional crystallisation has occurred in the Bakhuis belt, cumulates of mafic phases have to reside somewhere close to the
charnockites. Taken into account that the charnockite occurrence is not a local phenomenon but constitutes an area of about 30 by 30 kilometres *(see figure 2.4)*, an enormous amount of mafic cumulates needs to present somewhere. Besides the volumetrically subordinate mafic rocks present in the SW of the belt (i.a. the metagabbro), such a very large suite of mafic cumulates has not been found in the Bakhuis belt.

Hornblende dehydration melting of amphibolitic middle to lower crust is the proposed mechanism to create hornblende-rich I-type granites. The hydrous nature of the source rock generally precludes the generation of anhydrous, orthopyroxene bearing C-type magmas (Kilpatrick and Ellis, 1992 and references therein). Recently however, it has been argued that "normal" hornblende dehydration meting at a sufficiently high temperature is capable of producing charnockitic melts (Kar et. al., 2003; Kar and Bhattacharya, 2010). They base their hypothesis on a heavily deformed and metamorphosed charnockite occurrence in India. These particular charnockites however, lack many aspects typical of C-type magmas such as high K₂O and HFSE concentrations. Moreover, petrography does not unequivocally prove that orthopyroxene is a primary phase in these rocks. Geochemically, these authors provide sound evidence for melting in the presence of hornblende. Kar et. al. (2003) identify the protolith as hornblende-rich granulites that occur nearby the charnockites. This resembles the proximity of mafic granulites to the charnockites in the Bakhuis belt. An important difference however, is the REE-concentrations of the charnockites relative to the granulites: in the Bakhuis belt, the charnockites have a higher REE-content compared to the granulites. In the Indian case, the rare earth elements are more enriched in the granulites. This REE-depletion in the charnockites suggests that residual hornblende retains the REE in the source.

Experimental petrology is supportive of the potential derivation of orthopyroxene-bearing granitoids by hornblende dehydration melting (e.g. *Patino Douce and Beard 1995; Springer and Seck, 1997)*. All studies however result in granitoid melts with low (<2 wt%) potassium contents. Although suitable to explain the low-K Indian charnockites, this is in sharp contrast with the C-type magma and Bakhuis charnockites of which a high potassium-content is a fundamental feature. In fact, potassium enrichment during melting is favoured by decreasing H₂O-activity *(Ebadi and Johannes, 1991)*, suggesting that anhydrous melting is required to achieve the high K₂O-content of C-type magmas.

The main geochemical characteristic of the C-type magma is the high concentration of incompatible elements such as potassium, the REE and especially certain HFSE (Zr, Ti, P). High-temperature melting in the absence of water is of crucial importance in generating melts enriched in these elements. Increasing solubility of refractory phases such as apatite, zircon and ilmenite with temperature *(Harrison and Watson, 1983, 1984; Green and Pearson, 1986)* indicates dissolution of these phases is more effective in a hot melt than in a cold melt. Cold I-type granites are often saturated in respect to Zr-Ti-P as is for instance witnessed by the common occurrence of inherited zircon xenocrysts in these granites *(Miller, 2003)*. Higher melting temperatures therefore allow increased dissolution of apatite, zircon and ilmenite to the extent that they are not present in the residue. Hence, the high Zr-Ti-P concentrations of charnockites are consistent with melting at temperatures higher than normal I-type granites. Geothermometry (see section 7.3) confirms the high temperature character of the Bakhuis charnockites.

In the introduction it was argued that a high CO_2 -activity could lead to dehydration at the amphibolite-granulite facies transition due to amphibole breakdown without initiating partial melting *(Frost and Frost, 1987).* The resultant granulites are therefore (largely) dehydrated, but not melt depleted. During dehydration however, mobile elements can preferentially be lost from the protolith. Notoriously mobile elements such as rubidium and caesium might be affected, but also uranium and thorium can become mobile under CO_2 -rich conditions. Breakdown of hornblende and/or biotite can lead to the release of halogens, the presence of which has a large effect on U-Th mobility *(Keppler and Wyllie, 1990).* Depletion in the alkalis and U-Th is a feature characteristic of granulite terrains *(Rudnick and Presper, 1990)* and also highly common for charnockites, suggesting a genetic link between dehydrated granulites and C-type magmas. Moreover, experimental evidence suggests that minimum granitic melts become increasingly K-rich with lower H₂O-activity *(Ebadi and Johannes, 1991).* This provides another line of evidence in favour of melting at low H₂O-activities and high temperature to generate C-type magmas.

The discussion above indicates that high temperatures and a low H_2O -activity are critical in the formation of C-type melts. High incompatible element concentrations in charnockites indicate that a melt depleted source is untenable and a fertile source is required. Combining these observations led Kilpatrick and Ellis

(1992) to relate C-type magma generation to melting of dehydrated but fertile lower crust at temperatures higher than that witnessed by I-type granites. The same conclusion is reached in multiple other studies of charnockites highly similar to the C-type magma (Young et. al., 1997; Zhao et. al., 1997; Frost et. al., 2000). An important implication of this line of reasoning is that charnockites are not necessarily derived from a distinct source compared to I-type granites, but find their origin in different melting conditions. The protolith for I- and C-type magmas can therefore be identical. Zhao et. al. (1997) conclude that a subduction zone related basaltic-andesite is a good candidate for a charnockite source rock.

The model of melting a dehydrated but fertile granulitic source to generate a charnockitic magma is also the most appropriate solution for the Bakhuis charnockites. They are in many aspects very similar to the C-type magma: high K₂O and Zr-Ti-P concentrations but mobile element (Cs-Rb-U-Th) depletion. Melting of a fertile, dehydrated source at high temperatures is therefore compatible with the observed charnockite geochemistry. Whether the Bakhuis granulites match these source characteristics and if they represent the protolith of the charnockites, will be discussed in section 7.4.

7.2 – Petrogenesis of the Bakhuis charnockite suite

Quantitative modelling of melt evolution of the charnockite suite falls outside the scope of this research project, but the high-quality geochemical data do allow a qualitative assessment of the petrogenesis and evolution of the charnockitic melt. It is endeavoured to explain the major and trace element variation of the charnockite suite as a function of fractional crystallisation and assimilation (AFC) processes. Distinct trace element trends are suggestive of a relatively straightforward evolution of a parental charnockitic melt with a silica-content of ~ 65 wt% predominantly by fractional crystallisation.

Excluding the four intermediate charnockites with silica contents between 55 and 61 weight percent, the main charnockite suite ranges from 65 to 75 wt% SiO₂. As fractional crystallisation has the overall tendency to increase the silica content of the remaining melt, the samples with an SiO₂-content of 65 wt% are supposed to be the least evolved rocks. Therefore they are likely to most closely resemble the

parental charnockitic magma and hence these samples are used as a "starting composition" in the following arguments. The reason why the intermediate charnockite samples have not been selected, will become clear shortly.

Plagioclase fractionation is regarded to exert the most influence on the melt evolution based on the Ba/Sr versus silica variation (see figure 7.1). The barium/strontium ratio can be used to discriminate between alkali-feldspar and plagioclase fractionation. The budget of these two LIL elements is governed almost exclusively by feldspar. Strontium is incorporated in approximately equal amounts in both feldspars while barium is strongly incompatible in plagioclase but readily substitutes for K in alkali-feldspar. This implies that alkali-feldspar fractionation tends to decrease the Ba/Sr ratio of the melt while plagioclase fractionation has the opposite effect. Simultaneous fractional crystallisation of the two feldspars will result in a more or less constant Ba/Sr ratio. As is evident from figure 7.1, the Ba/Sr ratio of the charnockites increases with increasing silica-content and is predominant therefore indicative of plagioclase fractionation. The trend defined by the charnockite samples however, is not linear but becomes progressively steeper with SiO₂-



Figure 7.1 – Ba/Sr vs. SiO_2 diagram, modified after figure 5.6. Simplified two-stage model describing melt evolution by plagioclase fractional crystallisation. The red square is the presumed parental charnockite melt. Plagioclase compositions are indicated in the orange field (Deer et. al., 1992), the mafic granulites and gabbroic rocks plot in the purple field labelled "MG". Other symbols according to figure 5.1; see text for further explanation.

concentration. This development finds it origin in the thermodynamics of the albite-anorthite system. Anorthite occupies the high-temperature end of the solid solution between these two phases. Hence, early fractionating plagioclase will have a high An-content but will become more sodic with increasing fractionation (Winter, 2001). Due to the higher atomic weight of calcium compared to sodium, anorthite has a lower SiO₂-content than albite (see figure 7.1; plagioclase compositions after Deer et. al., 1992). A simple two-stage model is provided to illustrate this development. Upon cooling, the parental magma will start to precipitate plagioclase with a high anorthite component. The An-rich plagioclase has a Ba/Sr ratio close to zero and contains about 50 wt% SiO₂. Fractionation of this plagioclase will drive the composition of the remaining melt away from the plagioclase composition, towards higher Ba/Sr and SiO₂: stage 1 in figure 7.1. Cumulates containing high amounts of this early fractionating plagioclase will lie on a tieline between the parental melt (red square) and the plagioclase composition (orange field). After the melt has evolved to a silica-content of ~ 69 wt%, the composition of the fractionating plagioclase becomes more sodic ($An_{20}Ab_{80}$). Since a plagioclase with this composition contains about 64 wt% SiO₂, this increases the slope of the melt evolution trend: stage 2 in figure 7.1. Obviously, this model is an oversimplification since plagioclase composition will gradually change to more albitic compositions with melt evolution. This explains the arcuate trend of the charnockite suite in the Ba/Sr vs. SiO₂ diagram.

The four intermediate charnockites all fall on the early fractionation trend (stage 1) as described above. Based on the figure 7.1, their anomalously low silica-content can be explained by a simple plagioclase accumulation model. This diagram however masks another possibility: mixing with mafic granulites or the gabbroic samples. The composition of these mafic rocks is indistinguishable from anorthitic plagioclase in respect to silica and Ba/Sr: the purple ellipse in figure 7.1. The four intermediate charnockites can therefore also be the result of simple binary mixing of the parental magma with these mafic rocks by a process of assimilation. In figure 7.1, the distinction between plagioclase accumulation and assimilation can not be made.

Other elements do provide the opportunity to distinguish assimilation of mafic rocks on one side and crystal accumulation on the other side. Based on petrography, sample MKS 36 is believed to be enriched in plagioclase and zircon. Plotting zirconium versus silica should discriminate between zircon accumulation due to fractional crystallisation and assimilation based on large Zr-concentration differences between zircon and the mafic rocks. The opposite holds for plotting a highly compatible element versus silica. Assimilation of a mafic lithology with an inherently high compatible element concentration and fractionation of phases containing very low amounts of compatible elements should produce two contrasting trends. Figure 7.2 displays two of such diagrams. As is evident from this figure, the four intermediate charnockitic outliers fall into two highly different subgroups. Samples MKS 36 and 38 (dark blue diamonds) plot on crystal accumulation trends, line [2] in figure 7.2. The zirconium vs. silica diagram is consistent with accumulation of zircon in these samples. Note that plagioclase



Figure 7.2 – trace element variation diagrams showing the two processes responsible for the intermediate charnockite outliers: [1] binary mixing with mafic granulites or gabbroic rocks (purple field labelled MG); [2] crystal accumulation due to fractional crystallisation. The parental charnockite melt is indicated with a red square.

Symbols according to figure 5.1; **a)** zirconium vs. SiO₂, modified after figure 5.7; **b)** chromium vs. SiO₂, modified after figure 5.8. Note that due to the log-scale true binary mixing and accumulation lines are curved.

fractionation can not be distinguished in this diagram. These two samples have anomalously low Crconcentrations, indicating that accumulated phases (probably plagioclase and zircon) have a low chromium content. In contrast, the two other intermediate charnockites (MKS 14: open diamond; MKS 25: filled diamond) plot on a binary mixing curve with the compositional field defined by the mafic granulites and two gabbroic samples, line [1] in figure 7.2. This trend is in excellent agreement with mixing of the parental charnockite magma with a mafic lithology, probably by assimilation.

The interaction of samples MKS 14 and 25 with mafic rocks is not surprising given their field relationships and setting. Sample MKS 14 was taken near the Kilo Drie creek from a small, isolated forest outcrop where field relationships could not be identified. The nearby large outcrop at the Kilo Drie rapid showed evidence for the presence of large amounts of a metadoleritic lithology *(see section 4.1.1)*. This provides the possibility that either i) MKS 14 is a mixed sample of both the charnockite and the dolerite that was not recognised due to the poor exposure, ii) that the charnockitic magma locally assimilated part of the mafic lithology or iii) this sample is the result of mixing of a mafic (doleritic) and charnockitic magma. It is strange however, that sample MKS 15 taken less than 1 metre away from large mafic bands does not show any evidence for mixing or assimilation.

Sample MKS 25 was taken at Krong Soela in the close proximity of abundant mafic xenoliths *(see section 4.1.3)*. Given the fact that many of these granulitic xenoliths showed resorption textures at the xenolith-charnockite interface, assimilation of these mafic granulite xenoliths is a plausible explanation for the mixing trend seen in figure 7.2.

In contrast to typical I-type granites (see Zhao et. al., 1997 for a compilation), the Bakhuis charnockites are characterised by decreasing trace element concentrations with increasing silica-content. The rare earth elements, Zr, Nb, P_2O_5 and TiO₂ concentrations are all negatively correlated with SiO₂. This suggests that, unlike many I-type granites, accessory phases such as apatite (P_2O_5 , LREE), zircon (Zr, HREE) and ilmenite (TiO₂, Nb) are amongst the early fractionating phases. Besides the decreasing P_2O_5 with silica, apatite fractionation can also be inferred from the Eu-anomaly versus silica plot (see figure 5.6). As plagioclase fractionation has been established as the dominant control on melt evolution, the melt should become progressively depleted in europium. This should result in an increase in the europium anomaly with silica-content, which is not seen in figure 5.6; a clear trend is not present. Contemporaneous apatite fractionation however, will deplete the melt in rare earth elements. The two processes therefore counteract each other, annihilating the Eu-SiO₂ relationship.

 H_2O appears to be largely incompatible. This is reflected in the increased presence of hornblende in the most felsic samples (>70 wt% SiO₂) relative to the more intermediate samples (65-70 wt% SiO₂). It is therefore tempting to explain the two highly anomalous pyroxene-free samples MKS 17 and 35 as the last melt fraction to crystallise. These titanite and blue-green hornblende bearing samples do not share the common petrography of the charnockites, but are highly similar to the main charnockite suite in major and trace element geochemistry. On the basis of their silica-contents however (68-70 wt%), this explanation does not hold. Other mechanisms therefore need to be evoked to explain the occurrence of these two anomalous samples. A possibility is that these samples crystallised in a zone with locally increased H_2O -activity that potentially inhibits the stabilisation of pyroxene. Hornblende is in that case the obvious mafic phase to crystallise instead of pyroxene.

To summarise: the evolution of the charnockite suite can be satisfactorily explained by simple fractional crystallisation of plagioclase, accessory phases (apatite, zircon and ilmenite) and, on the basis of petrography, ortho- and clinopyroxene. Hornblende, when present, is usually a late-crystallising phase and is concentrated in the most felsic samples. The scatter seen in the major element data is most likely caused by small source heterogeneities and inefficient magma mixing. Two intermediate charnockites are confidently described by plagioclase and zircon accumulation. The other two intermediate outliers display sound field and geochemical evidence for assimilation of or mixing with mafic lithologies.

7.3 – Crystallisation temperature of the Bakhuis charnockites

Geological mapping during the 1970's revealed the ubiquitous presence of orthopyroxene in the Bakhuis granitoids, which supports their classification as charnockites. The anhydrous conditions required for the stabilisation of orthopyroxene imply melting at temperatures in excess of 900 °C (Robertson and Wyllie, 1971). Several methods have been used in this research project to quantify the crystallisation temperature of the charnockites, including petrography, whole rock saturation temperatures, ternary feldspar thermometry and titanium-in-zircon thermometry. The results of these methods have been discussed in the preceding chapters and will not be extensively repeated here. To summarise: petrography, whole rock saturation and ternary feldspar thermometry are in good agreement with each other and suggest crystallisation temperatures between 950 and 1000 °C. The titanium-in-zircon thermometer however, records temperatures that are on average ~100 °C lower. In this section, the apparent inconsistency of the different thermometers will be critically evaluated.

Zircon crystallisation temperatures obtained with the titanium-in-zircon thermometer are consistently lower than the whole rock zirconium saturation temperature. Experimental work has shown that the solubility of zircon in a melt is governed by temperature, Zr-concentration and composition of the melt *(Watson and Harrison, 1983).* The temperature at which zircon becomes saturated and starts to crystallise can be expressed as a function of these parameters. During melting, this saturation temperature dictates how much zircon from the protolith can be dissolved in the melt. In the case of zircon-undersaturated melts, saturation temperatures provide a minimum melting temperature. When the protolith contains more zircon than can be dissolved in the melt, zircon grains are often incorporated in the melt as xenocrysts. Hence, the presence and abundance of inherited zircon xenocrysts in a sample can be used as an indication whether the melt was saturated or undersaturated in respect to zircon *(Miller et. al., 2003).* Since not a single inherited grain was encountered during this zircon study, it can, despite the high whole rock Zr-concentrations (~150-450 ppm on average) be assumed that the charnockitic melt was not saturated in zircon. An obvious conclusion drawn from this observation is that the whole rock zircon saturation temperatures.

Recent work has indicated that zircon saturation is reached 50-100 °C above the whole rock saturation temperature since crystallisation of major phases in a cooling melt causes local oversaturation in Zr *(Harrison et. al., 2007)*. Moreover, the model by Watson and Harrison is applicable to hydrous systems containing at least 1.5-2 wt% H₂O. A felsic melt containing 0.2 wt% water will dissolve 30-40% less zircon than a hydrous melt *(Harrison and Watson, 1983)*. These lines of reasoning suggest that the onset of zircon fractionation should occur well above the whole rock saturation temperature, which is in strong contrast with the data presented in figure 6.6.

The discrepancy between the whole rock saturation and individual Ti-in-zircon crystallisation temperatures is difficult to explain. It is likely that one of the two approaches is incorrect. Whole rock zircon saturation temperatures rely on a well constrained Zr-content and major element composition of the melt. These parameters as they are measured in the bulk sample need not be similar to the melt from which the zircon crystallised. Sample MKS 36 and to a lesser extent MKS 38 appear to be enriched in zircon *(see sections 4.1.5 and 5.2.2).* Hence, whole rock zirconium concentrations for these samples are likely to be an overestimate, resulting in an erroneously high zircon saturation temperature. The other three samples however, do not display any evidence for significant fractional crystallisation or accumulation of zircon and are therefore less ambiguous.

Titanium concentrations in zircon are generally low (<30 ppm) and require sensitive and well calibrated detection methods. As is outlined in section 3.4.2.2, the LA-ICP-MS analyses of titanium was hampered by multiple problems. A small spot size was used, which resulted in low signal intensities. Additionally, the detection limit for Ti is approximately 6 ppm making Z91500 (Ti \approx 6 ppm) unsuitable as an external standard. This implies that: i) the titanium-contents of the zircons are close to the detection limit and consequently have large errors, and ii) there is no external check on the quality of the Ti-data. Simply discarding the titanium-data however, would be an oversimplification since the Ti-in-zrc temperatures correlate well and predictably with Hf-content, U/Th and Eu/Eu* (see section 6.3.3). The Ti-in-zrc thermometer is limited by the prerequisite of well constrained SiO₂ and TiO₂ activities in the melt from which the zircons crystallised. Figure 6.5 displays the influence of variable SiO₂ and TiO₂ activities on T_{Ti-in-zrc}. As is evident from this figure, decreasing SiO₂-activity lowers the T_{Ti-in-zrc} while decreasing TiO₂-activity positively affects T_{Ti-in-zrc}. Silica-activity can safely be assumed to be at or near unity and not have a significant effect on calculated temperatures.

are notoriously hard to quantify. The high whole rock TiO_2 -content and abundance of presumed Fe-Tioxides favour a high titanium activity. In the rare instance that all titanium was already precipitated in Tirich phases at the onset of zircon crystallisation, the TiO_2 -activity would be severely depressed. If this were to be the case, the calculated Ti-in-zrc temperatures would be underestimated by up to 120 °C. This scenario would explain both the low $T_{Ti-in-zrc}$ and the good correlation of the temperatures with melt evolution as this is not affected by the TiO_2 -activity. However, this scenario can hardly be reconciled with petrographic and geochemical evidence. The abundance of zircon in intermediate samples and apparent enrichment in for instance MKS 36, in conjunction with decreasing whole rock Zr and Hfconcentrations with silica-content, suggest that zircon is an early crystallising phase. Severe titaniumdepletion of the melt prior to zircon fractionation is therefore not a plausible explanation for the $T_{Ti-in-zrc}$ versus whole rock zircon saturation temperature discrepancy.

Unrealistic and inexplicably low temperatures obtained with the Ti-in-zrc thermometer have been reported elsewhere (see *Fu et. al., 2008* for a review). In addition to the issues described above, Fu et. al. specifically mention non-equilibrium behaviour of Ti-substitution as a possible cause. The principal substitution mechanism for titanium in zircon is the replacement of Si⁴⁺ by Ti⁴⁺ (*Harrison et. al., 2005*). This single substitution mechanism should not be influenced by concentrations of other elements as opposed to coupled substitution. However, titanium content appears to be correlated with Y, REE and P concentrations on the microscale (*Hofmann et. al., 2009*). This implies that trace element concentrations could exert an affect on titanium substitution and hence Ti-content in zircon. As a final note on the Ti-in-zrc temperatures: systematic analytical bias during LA-ICP-MS analysis cannot be excluded due to the lack of an external standard.

Estimation of melt temperature by whole rock saturation models of accessory phases is also potentially problematic. Saturation temperature models for apatite (*Harrison and Watson, 1984*) and zircon (*Watson and Harrison, 1983*) are dependent upon, amongst others, melt composition, water content and to a lesser extent pressure. These parameters can be difficult to quantify especially when fractional crystallisation changes the melt composition. Moreover, fractionation and non-equilibrium at the microscale can cause local oversaturation and precipitation of phases well above their predicted whole rock saturation temperature (*Harrison et. al., 2007*).

The difference in chemistry between charnockites and most other granitoids can also introduce errors in bulk rock saturation models. Models for apatite and zircon saturation have been experimentally determined for typical granitoid compositions. The lower water content of charnockites can have a major effect on dissolution kinetics and drastically alter saturation temperatures. For these reasons, whole rock saturation temperatures should be regarded with caution. They can be used to confirm independent geothermometers but should not be treated as undisputable evidence for melt temperatures by itself.

Of the techniques employed in the quantification of melt temperatures for the Bakhuis charnockites, ternary feldspar thermometry appears to be most reliable. The ternary feldspar geothermometer is often used, well calibrated and has demonstrated its reproducibility and accuracy. Replicated results for multiple grains in two samples are in excellent agreement with each other and record temperatures between 940 and 990 °C (see section 5.4). The main criterion for the application of this thermometer to the Bakhuis charnockites to establish crystallisation temperatures, is that the feldspars are truly magmatic and exsolution is not the result of subsequent metamorphic overprint. Convincing evidence for a magmatic origin of the analysed feldspar grains is provided by the occurrence of plagioclase phenocrysts with antiperthitic exsolution in the rims in the same thin section. If exsolution was caused by metamorphic recrystallisation, the whole grain would have been affected rather than solely the rim.

Other petrographic indications of high crystallisation temperatures are provided by the occurrence of blue HT quartz and rare inverted pigeonite (see section 4.1.2). The minimum exsolution temperature for pigeonite is 950 °C for highly ferroan compositions (e.g. Ranson, 1986) indicating melt temperatures close to 1000 °C for sample MKS 22. This is in agreement with estimates derived from whole rock apatite saturation temperatures (see section 5.1) and confirmed by ternary feldspar thermometry. As discussed in detail, titanium-in-zircon thermometry yields spuriously low temperatures for zircon crystallisation. Whether this is caused by ill constrained geological processes or analytical bias remains unclear, but questionable Ti-in-zrc data have been reported more often. On this basis, little significance is awarded to the Ti-in-zircon temperatures. Results obtained with the ternary feldspar thermometer are regarded as the best approximation of melt temperatures of the Bakhuis charnockites, which are between 940 and 990 °C.

7.4 – The source of the charnockitic melt

The key question of this research project is: are the charnockites related to the ultrahigh-temperature metamorphism by syn-metamorphic partial melting of the granulites? The timing of charnockite magmatism precludes this scenario, as will be discussed in the next section. The younger age of the charnockites however, does not necessarily imply that the two suites are not genetically related. In this section, relevant trace element and radiogenic isotope evidence will be presented to put constraints on the composition of the charnockites source and potentially relate it to the granulites, metadolerites or metagabbro.

Rare earth element concentrations and patterns can be highly useful in obtaining information on the source rock of melts. Common accessory phases such as apatite, zircon, hornblende and titanite exert the dominant control on the rare earth element budget in crustal rocks. Although these phases all incorporate REE, they each tend to prefer certain rare earth elements over the others. The heavy REE for instance are highly compatible in garnet and zircon while these phases strongly exclude the light rare earth elements. Apatite on the other hand prefers the LREE while the middle REE are preferentially included in hornblende and titanite. These phases can be strongly retentive of their preferred REE during melting. A magma extracted from a protolith with residual garnet for example will be strongly HREE depleted as these elements are held back in the garnet.

The Bakhuis charnockites do not exhibit rare earth element patterns indicative of major REEbearing residual phases. Rare earth element concentrations are high and the La/Yb_N slopes are typical of most subduction related magmas. Some samples (e.g. MKS 30) do exhibit a mild flattening in the light REE, which might indicate that this sample has lost some apatite due to fractional crystallisation. No heavy REE depletion suggestive of residual garnet is present in any of the samples; nor are the MREE or yttrium depleted and hence hornblende is not considered to be of influence during melting. In contrast, the anomalous metamorphic sample MKS 56 does show a REE-pattern indicative of residual hornblende. It is characterised by a positive HREE and negative LREE slope, leading to a marked depression at dysprosium-holmium. As this sample is considered to be a leucosome, this REE-pattern suggests that it is a partial melt from a hornblende-bearing protolith.

As a general conclusion, the rare earth element data do not provide any evidence for a hornblende or garnet bearing source. It must be noted however, that the REE influence described above is only valid if the phase is residual. Complete melting of for instance a hornblende-bearing protolith will liberate all REE to the melt. Hence, the rare earth pattern of this melt will show no signs of hornblende as a residual phase. Nevertheless, the rare earth data put an important constraint on the charnockite source: no residual hornblende is present. As described in chapter 4, the mafic granulites, metadolerites and metagabbro contain abundant hornblende. This argues against their involvement in charnockite generation unless the degree of partial melting was sufficient to break down all hornblende. The intermediate granulites are on average hornblende-poor compared to their mafic counterparts and are therefore a more likely candidate.

The most conspicuous geochemical difference between the granulites and charnockites is formed by their highly distinctive K_2O vs. SiO₂ trends *(see figure 5.2)*. The charnockites contain up to 5.5 wt% potassium for the most silica-rich samples, while the granulites define a less steep trend at ~1.5 wt% K₂O at maximum. A similar difference is present for other alkali metals, as the granulites contain up to 10 times less rubidium and caesium. Although anhydrous melting favours the release of potassium into the melt *(Ebadi and Johannes, 1991; see section 7.1.2)*, it remains questionable whether partial melting of the granulites can produce a relatively K-rich charnockitic melt.

Three scenarios can explain the alkali-poor composition of the granulite suite. It is generally assumed that the protolith of the granulites consists of supracrustal sediments and volcanics derived from the TTG-greenstone belt to the north. Low-potassium (<1 wt% K₂O at 60 wt% SiO₂) arc magmas are not uncommon (e.g. *Winter, 2001)* and have also been recognised in the Guiana TTG-greenstone belt (*E. de Roever, pers. comm.*). Hence, the low alkali nature of the granulites can be inherited from the original magma composition. Secondly, dehydration under CO₂-rich conditions can cause severe depletion in mobile elements such as alkali metals, uranium and thorium (see section 7.1.2). Finally, it is possible that, despite the endeavour to sample fertile granulites, these samples did experience some melt extraction and hence lost part of their potassium content.

Too little geochemical data is present to unambiguously favour one of these explanations. In the light of the consistently lower incompatible trace element and potassium concentrations of the granulite

suite compared to the charnockites, it appears plausible that the granulites suffered from dehydration in combination with some melt extraction. However, in section 7.1.2 it was argued that the charnockite source rocks where dehydrated, but still fertile. This could indicate that the restitic nature of the granulites is caused by charnockite extraction. The large (>50 km) distance between the charnockite occurrence and the sampling sites of the granulite suite (Blanche Marie and drill core LA 156) precludes this possibility. However, a limited amount of charnockitic melt was produced contemporaneously with UHT-metamorphism in the northeastern part of the belt. Alternatively, the granulites experienced minor melting during metamorphism, as witnessed by the presence of leucosomes in the Blanche Marie area. In this scenario, a second phase of more extensive melting is proposed to generate the charnockites. In either case, melting experiments or modelling are required to determine whether melting of the K-poor intermediate granulites can produce the charnockite melt.

At the end of the trace element data presentation in chapter 5, two element-ratio variation diagrams were shown. The objective of these plots was to use elemental ratios that were not likely to fractionate during partial melting as a proxy for the source composition. The diagram that yielded the best results is reproduced in figure 7.3. In this plot, the Ce/Sr ratio is plotted against the Zr/Hf ratio of the Bakhuis sample suite. Zirconium over hafnium was selected since tight constraints can be put on the behaviour of both elements during partial melting. These two elements are highly incompatible and their total budget in a rock is governed almost solely by the mineral zircon. As discussed in section 7.3, the complete lack of inherited zircon encountered during the zircon in situ study suggests that the charnockite melt was undersaturated with respect to zircon (Miller, 2003). An undersaturated melt is very hard to reconcile with residual zircon and all Zr and Hf can be assumed to have dissolved into the melt. Fractionation of these two elements is therefore highly unlikely and the ratio of Zr/Hf of the melt must be identical to that of the protolith. Cerium over strontium was chosen as these two elements have similar partition coefficients during melting (Rollinson, 1993). Residual plagioclase can hold back significant quantities of strontium leading to Ce-Sr fractionation during melting. The cerium budget is principally controlled by accessory phases such as apatite. Nevertheless, a clear separation between the charnockites and intermediate granulites on one side and the mafic granulites and gabbroic samples on the other side is achieved in figure 7.3. The charnockite samples span a large range of Ce/Sr and Zr/Hf, that can be explained by plagioclase and zircon fractionation. Fractional crystallisation of these phases will increase the Ce/Sr of the melt as strontium is incorporated in plagioclase and cause a decrease in Zr/Hf as zircon occupies the high-temperature end in the zircon-hafnon solid solution. Accumulation of these phases has the opposite effect.



Figure 7.3 – Ce/Sr vs. Zr/Hf plot for the Bakhuis sample suite (modified after figure 5.14). Symbols according to figure 5.1; inverse green triangles represent intermediate granulites. The dashed orange field covers the mafic granulites and gabbroic samples, the green field includes the intermediate granulites and the charnockites fall into the blue field. See text for further explanation. In section 7.2 it was argued that samples MKS 36 and 38 have experienced combined plagioclase-zircon accumulation. This is corroborated by figure 7.3 where these samples plot towards higher Zr/Hf and lower Ce/Sr along the fractionation trend. Sample MKS 30 also plots in this zone, which is consistent with the above average Zr-content of this sample *(see figure 5.7)*. The parental charnockite melt as defined in section 7.2 has a Ce/Sr ratio of 0.35 ± 0.08 and a Zr/Hf of 44 ± 4 . This is in good agreement with the composition of the intermediate granulites. They show a large range in Ce/Sr ratios but are remarkably uniform with respect to Zr/Hf. The anomalous sample MKS 56 has not been included in the range.

The intermediate granulites and charnockites differ significantly from the narrow range in compositions defined by the dolerite, metagabbro and mafic granulites. These plot at lower Ce/Sr (0.09 ± 0.05) and Zr/Hf (33 ± 5) compared to charnockite-intermediate granulite trend. Based on this diagram, it can therefore be concluded that the intermediate granulites are in good agreement with the composition of the inferred parental charnockite melt. In other words, melting of the intermediate granulites is likely to produce a melt with Ce/Sr and Zr/Hf similar to that of the charnockites. Even by itself, the well constrained Zr/Hf ratio justifies this conclusion: the mafic granulites consistently have a lower Zr/Hf than the charnockites.

In addition to the potential source discrimination, figure 7.3 also provides additional support for the mixing or assimilation relationship between sample MKS 25 and a mafic lithology. This sample plots on a mixing curve between the parental charnockitic melt composition and the field of mafic granulites with a composition intermediate between the two end members. Sample MKS 25 is joined on the mixing line by the other Krong Soela sample MKS 26.

Based on the trace element data, a preliminary conclusion can be drawn that the intermediate granulites more closely approximate the charnockite source than do the mafic granulites, dolerite or metagabbro. The radiogenic isotopes presented in figure 5.15 are however, at odds with this conclusion. As already discussed in section 5.3, the use of radiogenic isotopes in constraining the source of the charnockite suite is impeded by the juvenile nature of the entire Bakhuis system. The time span between extraction from the mantle in an arc system, via erosion and sedimentation to granulite metamorphism covers less than 200 Ma. As a consequence, the development of a crustal isotopic signature had only just started for the granulites. It is therefore very difficult, on an age of \sim 2000 Ma, to distinguish between a juvenile component and a very young crustal component. An additional disadvantage of the present isotope study is the lack of high-precision parent-daughter ratio determinations. Instead of time consuming isotope dilution analysis, XRF and ICP-MS derived values were used.

Despite these limitations, the Sr-Nd isotopic data do allow an important conclusion to be drawn: the initial strontium isotopic signature of the charnockites is different outside error from the intermediate granulites analysed in this study, but is identical to both the mafic granulites and gabbroic samples. This is in strong contrast with the conclusions based on the trace element data posed above. Initial neodymium isotope ratios of the charnockites, granulites and gabbroic rocks are within error of each other and do no provide any conclusive evidence.

There are two arguments to explain the discrepancy between the Rb-Sr isotopes and trace elements. As mentioned in section 5.3.2, the Rb-Sr system of the charnockites has probably experienced an episode of resetting after crystallisation. This could explain the erroneously low initial ⁸⁷Sr/⁸⁶Sr ratios of at least part of the charnockites; it is possible that the actual ⁸⁷Sr/⁸⁶Sr ratio during crystallisation was higher. In addition, the strontium isotope composition of the intermediate granulites is based on only three samples and therefore potentially not representative. Rubidium-strontium data obtained on 28 intermediate and felsic granulites from the central part of the Bakhuis belt by Priem et. al. (1978) display considerable scatter in initial ⁸⁷Sr/⁸⁶Sr ratios, ranging from 0.7023 to 0.7035. The lowest of these ratios overlap within error with initial ratios of the mafic granulites, metadolerite and metagabbro, and also with the most reliable charnockite samples. Hence, the dissimilarity between the intermediate granulites and charnockites could be caused by non-representative analyses of the granulites.

7.5 – The relationship between the charnockite magmatism and UHT-metamorphism

The orthopyroxene-bearing granitoids present in the Bakhuis belt have been interpreted as a direct consequence of the ultra-high temperature metamorphic event at 2.07-2.05 Ga. It was suggested that the charnockites formed contemporaneously with the granulite metamorphism by partial melting of these granulites. In other words: the UHT-metamorphism was accompanied by partial melting. A direct implication of this hypothesis is that the crystallisation age of the charnockites should be identical to the age of metamorphism. This research project was dedicated to confirming or disproving the synmetamorphic origin of the charnockites. Zircon uranium-lead dating provided unambiguous evidence that the current hypothesis is incorrect; charnockite magmatism occurred >70 Myr after peak metamorphic conditions at around 1975 Ma. Hence, the hypothesis needs revision. In my opinion, two scenarios are possible: i) the age determination of UHT-metamorphism is incorrect, or ii) metamorphism and charnockite magmatism occurred during two separate events.

Doubts can be raised on the timing of granulite metamorphism. Zircon geochronology on metamorphic samples is notoriously difficult due to the potential analysis of mixed grains with a magmatic core overgrown by a metamorphic rim. De Roever et. al. (2003) employed the zircon lead-evaporation method to establish the timing of metamorphism (2.07-2.05 Ga). As with to all other whole-grain zircon dating techniques, the Pb-evaporation method has to overcome more analytical challenges than in situ techniques. Zircon grains need to be flawless as any lead contamination in cracks can cause spurious ages. In addition, it is impossible to date a single zone within a grain and mixed analyses could cause erroneously old ages. The age of metamorphism is based on only two Pb-Pb ages of clearly metamorphic samples. Per sample, four to five grains were analysed. Multiple grains provided only a single heating step. Moreover, successive heating steps of a single sample often display an increase in Pb-Pb age. The obtained age data could therefore be the result of mixing between a metamorphic rim and an inherited magmatic core.

In support of the ages obtained by De Roever et. al. (2003) are Pb-evaporation ages obtained on the charnockite in the northeastern part of the belt (2065 Ma) and three pegmatite layers (2059-2081 Ma). One of these pegmatites however, also contains two zircons with an age of ~1980 Ma (based on two and four heating steps), which is identical to the charnockite age. The Pb-evaporation dating of two synkinematic metadolerite dikes also provides support that the Pb-Pb ages of the granulites are correct. Ages of 2056 and 2060 Ma were obtained for these samples. Since zircon inheritance is very hard to argue for in juvenile mafic magmas, these ages can safely be assumed to record the timing of intrusion. Zircon Pb-evaporation ages of the two granulites are confirmed by SHRIMP and SIMS data of these samples (J.M. Lafon, unpublished confidential data). However, as these data have not been published nor is any additional information on the analyses available, these ages should be treated with caution. In theory, they could be the result of a mixed analysis of an original magmatic component and a younger metamorphic overgrowth. Although lead diffusion is normally very slow in zircon (e.g. Lee et. al., 1997; Cherniak and Watson, 2000), the metamorphic temperatures in excess of 950 °C could have led to homogenisation of lead concentration and isotope composition in the zircons.

Nevertheless, it is difficult to challenge the metamorphic zircon ages as multiple individual samples, metamorphic and magmatic, analysed using different techniques yield consistent ages.

A more plausible explanation for the discrepancy between the charnockite and metamorphic ages, is that the magmatism and metamorphism are two separate events. The hypothesis investigated in this thesis is predominantly based on the similarity in PT-conditions of the two events; linking the UHTmetamorphism to high-temperature magmatism appeared very reasonable. The accurate zircon U-Pb ages reported in this thesis however, clearly preclude this possibility if the age for the metamorphism is accepted (see above). Instead, the timing of charnockite magmatism is contemporaneous with a magmatic pulse leading to the emplacement of the leucogranites and metavolcanics in western Suriname (see section 2.2). This magmatic pulse has also affected the Bakhuis belt as demonstrated by the 1980 \pm 5 Ma anorthosite body in the core of the belt (De Roever et. al., 2003). Moreover, the charnockite U-Pb age is within error of timing of metamorphism in the Coeroeni granulite terrain. In contrast, the biotite granites that constitute the dominant lithology surrounding the belt, have been emplaced ~40 Myr later at 1949 \pm 12 (De Roever et. al., in preparation). The distinct ages of metamorphism and charnockitic magmatism however, do not implicitly preclude a possible relationship of the charnockitic melt to the granulites. As discussed in the previous section, a genetic link between the two suites is not unequivocally established, although trace element data strongly suggest such a relationship. Another unresolved point is the origin of the gabbroic lithologies (the metadolerites and metagabbro) present in the southwestern part of the Bakhuis belt. At first, these were considered to be related to the single metamorphic-magmatic event. The metadolerite xenoliths encountered in the charnockites and the metadolerite dikes in the granulites were assumed to be derived from the same juvenile source. In addition, the metagabbro was regarded as a coarse-grained equivalent of this mafic melt. Were the charnockites to be contemporaneous with the UHT-metamorphism, the geodynamics of the Bakhuis belt would have been easily explained. The emplacement of juvenile mafic magma underneath the supracrustal sequence would provide the heat required for the ultrahigh-temperature metamorphism. Release of large amounts of CO_2 from this mafic underplate could explain the dehydration of the granulites without inducing melting. Ultimately, PT-conditions became sufficiently high that the solidus was reached, leading to partial melting of the supracrustal granulites to form the charnockitic melt.

In the light of the new geochronological timeframe, this model needs refinement. The timing of mafic magmatism remains unconstrained as insufficient data are available to distinguish the different mafic rocks present in the belt. The metadolerite and metagabbro show marked geochemical differences but are compositionally similar to the range defined by the mafic granulites. It is possible that they were emplaced during separate events. A first stage of mafic magmatism could have resulted in the UHT-metamorphism and intrusion of synkinematic dolerite dikes. About 70 Myr later, a second stage of basaltic magmatism could have resulted in partial melting of the granulites to form the charnockites and emplacement of the metagabbro and metadolerites. Field relationships, albeit ambiguous, suggest that the charnockites are intrusive in the metagabbro. This favours the explanation that the metadolerite and metagabbro are part of the first mafic pulse and that the charnockites are simply intrusive in them. A detailed geochemical and isotopic study in combination with dating of the metagabbro is required to elucidate this subject.

The presence of synkinematic dolerite dikes in the granulite suite constitutes sound evidence that mafic magmas were present at the time of ultrahigh-temperature metamorphism. It is likely that this hot, anhydrous basaltic melt provided the heat necessary for the high geothermal gradient indicated by PT-estimates. Moreover, the counter-clockwise PTt-path of the granulites (*De Roever et. al., 2003*) is in excellent accordance with mafic underplating. So far, this appears to be a highly plausible scenario for the geodynamical framework of the UHT-metamorphism and is in line with the discussion on the evolution of the Guiana shield by Delor et. al. (2003).

It is however, difficult to explain the second phase of high-temperature anhydrous melting some 70 Myr later. A possible explanation is a renewed pulse of voluminous mafic magmatism at about 1980 Ma causing an increase in the geothermal gradient. This in turn resulted in large scale granulite metamorphism in the Coeroeni area, charnockite intrusion and granitic magmatism in western Suriname. It is however difficult to imagine how a new pulse of basaltic magma could cause melting of the granulites while the older underplate was still present. The older slab of basaltic crust should provide a blanket for the granulitic middle crust. A possibility is that sinistral shearing *(see section 2.3)* continued after UHT-metamorphism and underplating, and that the doming of the Bakhuis belt caused a window to open in the mafic slab. A renewed pulse of basalt injection could therefore cause anhydrous melting in this slab window leading to charnockitic magmatism. In contrast, the increased geothermal gradient could cause regional melting of the older mafic slab to produce the leucogranites and metavolcanics.

An alternative model for the second phase of high temperature conditions is mantle upwelling due to delamination of the basaltic slab (e.g. *Elkins-Tanton, 2005; Wang et. al., 2007)*. In this process, either dehydration of the delaminated slab, upwelling of hot, anhydrous asthenosperic mantle or a combination of the two can initiate melting. Lithospheric delamination is favoured by regions characterised by a young crust that has been weakened by a previous high-temperature event (*Elkins-Tanton, 2005*). The Guiana shield is an excellent example of such a region. The delamination model is attractive for several reasons. First, it easily explains the combined anhydrous charnockite and normal granitic magmatism by asthenospheric upwelling dominated versus dehydration melting dominated domains in the lower crust. Hence, it is also compatible with the granulite facies metamorphism in the Coeroeni area. Finally, delamination will lead to crustal rebound and uplift, thereby potentially facilitating the exhumation of the Bakhuis belt.

Chapter 8 – Concluding remarks

8.1 - Conclusions

The Bakhuis charnockites form a coherent suite of orthopyroxene-bearing granitoid rocks in the Bakhuis granulite belt, western Suriname. Their characteristic petrography closely resembles the typical charnockite-type (C-type) magma. Next to the invariable presence of orthopyroxene, a high crystallisation temperature is suggested by the general scarcity of hornblende and the presence of ternary feldspar. In the least deformed samples, the rare occurrence of inverted pigeonite and blue quartz offers additional support for a high temperature melt. Whole rock apatite and zircon saturation temperatures corroborate the textural evidence and quantitative ternary feldspar geothermometry yields crystallisation temperatures between 940 and 990 °C. In contrast, temperatures obtained with the titanium-in-zircon thermometer are consistently much lower. Although processes that could cause this discrepancy are evaluated, a fully satisfactory explanation has yet to be found.

Whole rock geochemistry suggests that the major and trace element variation of the Bakhuis charnockite suite can be explained by relatively simple evolution of a parental magma of about 65 weight percent SiO₂. Although some scatter in the variation diagrams is probably caused by source-heterogeneity, evolution of the melt occurred predominantly by fractional crystallisation of plagioclase, zircon, ilmenite and apatite. Cumulitic samples enriched in zircon and plagioclase were recognised on the basis of petrography and geochemical trends. Two samples show clear evidence of interaction with a mafic lithology, either mafic granulites or igneous rocks. Contamination of these samples can have occurred either by magma-mixing or wall rock assimilation; the limited field evidence is in favour of the latter. Major and trace element compositions are also in line with the typical C-type magma, which is distinct from I- and A-type granites by high K₂O, TiO₂, P₂O₅ and Zr concentrations and mobile element (Cs, Rb, Th, U) depletion. The C-type magma does not inherit its characteristic composition from a different source compared to I-type granites, but rather from abnormal melting conditions. Experimental and geochemical evidence suggests that charnockitic melts are generated by partial melting of a fertile but dehydrated granulitic crust in the general absence of water. The increased temperature favours the dissolution of Zr-Ti-P-rich accessory phases that are normally residual during I-type granite extraction. The highly potassic character of the charnockites is caused by the low H₂O-activity, which shifts the minimum melt to more K₂O-rich compositions.

The hypothesis assessed in this thesis is that the charnockites are related to an episode of ultrahightemperature metamorphism in the Bakhuis belt. Based on the high-temperature character of the charnockites, it was suggested that UHT-metamorphism was accompanied by partial melting. Hence, it is hypothesised that the source of the charnockitic melt is formed by the metamorphic granulites. This suite of rocks is characterised by ubiquitous compositional banding and consists of 50-55% intermediate granulites (in general opx, cpx, plagioclase, quartz and minor hornblende), 35% mafic granulites (opx, cpx, hornblende and plagioclase) and 5-10% pelitic and 5% miscellaneous felsic lithologies. The presence of mafic granulite xenoliths in the charnockitic rocks indicates that the charnockites are intrusive in the metamorphic suite. A restitic appearance of some xenoliths suggest potential derivation of the charnockites as partial melts of the granulites. Coarse and fine-grained hornblende-rich magmatic rocks of basaltic composition are found to occur in direct contact with the charnockites. Although field relationships point towards intrusion of the charnockites in these gabbroic rocks, a comagmatic origin as two immiscible magmas can not be excluded completely. Geochemically, the gabbroic bodies are indistinguishable from the mafic granulites but texturally they are highly contrasting.

With respect to the source of the charnockitic melt, trace element data are in agreement with derivation from the hornblende-poor intermediate granulites and metapelitic lithologies. Initial Sr-Nd isotopic signatures however, do not confirm this explanation. The intermediate granulites plot outside error of a tight isotopic range defined by the charnockites, mafic granulites and two magmatic gabbroic samples encountered in the charnockite suite. All lithologies however have initial ratios very close to bulk Earth, indicative of a juvenile source. Neodymium model ages support this conclusion as no evidence for an Archaean component in either the granulites or charnockites is distinguished. Based on the high-quality trace element data, it is concluded that melting of the intermediate lithologies to produce the charnockites is more plausible than preferential melting of mafic granulites or gabbroic rocks. Overall, whole rock geochemistry supports the above mentioned hypothesis. High-precision zircon U-Pb dating of five charnockite samples however, reveals that charnockite magmatism postdates UHT-metamorphism by approximately 70 Myr. Uranium-lead upper intersect discordia ages range from 1959 to 1986 Ma, which is in sharp contrast with the timing of metamorphism at 2.07-2.05 Ga. The three most reliable samples yield ages identical within error at around 1980 Ma. As a consequence, these new U-Pb ages of the charnockites provide solid grounds for rejecting the hypothesis. A direct implication is that there is currently evidence for two consecutive ultrahigh-temperature events in the Bakhuis belt. The metagabbroic rocks and metadolerites typical of the Bakhuis belt are regarded to play a crucial role in either one or both of these events.

A major unresolved issue is the timing of mafic magmatism. Synkinematic metadolerite dikes are common in the granulite suite, but metagabbroic bodies are also encountered in close contact with the charnockites. Primarily based on the scarce field relations and general lack of evidence for interaction of the charnockitic melt with the mafic lithologies, the most plausible solution is that the metagabbro and metadolerites are all emplaced during a single magmatic phase at the time of UHT-metamorphism. Mafic underplating is an efficient source of heat and CO₂ required for ultrahigh-temperature metamorphism. Hence, pooling of hot, anhydrous basaltic magma underneath the Guiana crust at 2.07-2.05 Ga is probably the direct cause of metamorphism of the supracrustal protolith. Local migmatisation occurred, as is witnessed by the presence of leucosomes in the granulite suite. However, the geotherm was not sufficiently raised to allow significant partial melting during metamorphism and voluminous charnockite generation. A next stage of thermal perturbation postdating the UHT-metamorphism by about 70 Myr, has caused partial melting of the dehydrated but fertile intermediate granulites in the southwestern part of the Bakhuis belt. Besides the charnockite intrusion, granulite facies metamorphism of the Coeroeni area and granitic magmatism in western Suriname can all be related to this phase at approximately 1980 Ma. Delamination of the mafic underplate emplaced prior to UHT-metamorphism provides an attractive explanation for this second ultrahigh-temperature stage.

8.2 – Suggestions for future research

As already hinted above, the trace element and isotopic constraints on the composition of the charnockite source rock are not optimal. In depth geochemical modelling or melting experiments of the granulite suite could shed more light on this issue. Radiogenic isotopes are the most established method in discrimination between different source rocks. The reason that the isotope study in this thesis proved not to be so fruitful, is twofold. The juvenility of the Guiana shield implies that isotopic variations are small. The supracrustal granulites have received little time for the development of a crustal isotopic signature prior to metamorphism and charnockite magmatism. Hence, it is difficult to distinguish between a juvenile melt derived from an enriched mantle source and a very young crustal component. Secondly, using XRF and ICP-MS derived parent-daughter ratios resulted in large uncertainties on initial isotope ratios. Moreover, the Rb-Sr system appears to have suffered from resetting after crystallisation. Isotope dilution analyses of the current sample set might provide the desired resolution to distinguish between the subtly different potential source rocks.

The origin of the various magmatic mafic lithologies in the Bakhuis belt should form a prime subject of future research. Most likely, the mafic magmas have played a fundamental role as a potential heat source in the development of the UHT-belt and possibly the high-temperature charnockite magmatism. The data in this thesis are not conclusive whether the synkinematic dolerite dikes in the granulites, doleritic xenoliths and gabbroic bodies are all related to the same mafic source and magmatic pulse. A detailed trace element and isotopic study of these mafic lithologies is therefore recommended. Hafnium isotopes in particular have the potential to provide clarity on this matter. The Lu-Hf decay system is highly similar to the Sm-Nd system in terms of parent-daughter fractionation, but the shorter half-live of lutetium could provide the age resolution required to distinguish between different mafic pulses. As the timing of mafic magmatism is crucial in unravelling this problem, dating of the gabbroic bodies can provide valuable new evidence.

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References

- Almeida, M.E., Macambira, M.J.B. and Oliveira, E.C. (2007); Geochemistry and zircon geochronology of the I-type high-K calc-alkaline and S-type granitoid rocks from southeaster Roraima, Brazil: Osrosirian collisional magmatism evidence (1.97-1.96 Ga) in central portion of Guyana Shield; *Precambrian Research* 155 p. 69-97
- Anczkiewicz, R., Oberli, F., Burg, J.P., Villa, I.M., Günther, D. and Meier, M. (2001); Timing of normal faulting along the Indus Suture in Pakistan Himalaya and a case of major ²³¹Pa/²³⁵U initial disequilibrium in zircon; *Earth and Planetary Science Letters* **191-2** p. 101-114
- Begemann, F., Ludwig, K.R., Lugmair, G.W., Min, K., Nyquist, L.E., Patchett, P.J., Renne, P.R., Shih, C.Y., Villa, I.M. and Walker, R.J. (2001); Call for an improved set of decay constants for geochronological use; *Geochimica et Cosmochimica Acta* 65-1 p. 111-121
- Ben Othman, D., Polvé, M. and Allègre, C.J. (1984); Nd-Sr isotopic composition of granulites and constraints on the evolution of the lower continental crust; *Nature* **307** p. 510-515
- Bhattacharya, S. (2010); Review: the charnockite problem, a twenty first century perspective; *Natural Science* **2-1** p. 402-408
- Brown, M. (2006); Duality of thermal regimes is the distinctive characteristic of plate tectonics since the Neoarchean; *Geology* **34-11** p. 961-964
- Brown, M. (2007); Metamorphic conditions in orogenic belts: a record of secular change; *International Geology Review* **49-3** p. 193-234
- Chang, Z., Vervoort, J.D., McClelland, W.C. and Knaack, C. (2006); U-Pb dating of zircon by LA-ICP-MS; *Geochemistry Geophysics Geosystems* **7-5**
- Cherniak, D.J. and Watson, E.B. (2000); Pb diffusion in zircon; Chemical Geology 172 p. 5-24
- Cherniak, D.J. and Watson, E.B. (2007); Ti diffusion in zircon; Chemical Geology 242 p. 470-483
- Collins, W.J., Beams, S.D., White, A.J.R. and Chappell, B.W. (1982); Nature and origin of A-tupe granites with particular reference to southeastern Australia; *Contributions to Mineralogy and Petrology* **80** p. 189-200
- Collins, W.J. (2002); Hot orogens, tectonic switching, and creation of continental crust; *Geology* **30-6** p. 535-538
- Creaser, R.A., Price, R.C. and Wormald, R.J. (1991); A-type granites revisited: assessment of a residualsource model; *Geology* **19** p. 163-166
- Deer, W.A., Howie, R.A. and Zussman, J. (1992); An introduction to the rock-forming minerals; 2nd edition, Pearson Prentice Hall, 696 p.
- Delor, C., Roever, E.W.F. de, Lafon, J.M., Lahondère, D., Rossi, P., Cocherie, A., Guerrot, C. and Potrel, A. (2003); The Bakhuis ultrahigh-temperature granulite belt (Suriname): II. implications for late Transamazonian crustal stretching in a revised Guiana Shield framework; *Géologie de la France* **2-3-4** p. 207-230
- DePaolo, D.J. (1981); Neodymium isotopes in the Colorado Front Range and crust-mantle evolution in the Proterozoic; *Nature* **291** 193-197
- Dickin, A.P. (2005); Radiogenic Isotope Geology; 2nd edition, Cambridge University Press, 492 p.

- Duchesne, J.C. and Wilmart, E. (1997); Igneous charnockites and related rocks from the Bjerkreim-Sokndal layered intrusion (Southwest Norway): a jotunite (hypersthene monzodiorite)-derived Atype granitoid suite; *Journal of Petrology* **38-3** p. 337-369
- Ebadi, A. and Johannes, W. (1991); Beginning of melting and composition of first melts in the system Qz-Ab-Or-H₂O-CO₂; *Contributions to Mineralogy and Petrology* **106** p. 286-295
- Eggins, S. and Hensen, B.J. (1987); Evolution of mantle-derived, augite-hypersthene granodiorites by crystal-liquid fractionation: Barrington Tops Batholith, eastern Australia; *Lithos* **20** p. 295-310
- Elburg, M., Vroon, P, Wagt, B. van der and Tchalikian, A. (2005); Sr and Pb isotopic composition of five USGS glasses (BHVO-2G, BIR-1G, BCR-2G, TB-1G and NKT-1G); *Chemical Geology* 223-4 p. 196-207
- Elkins-Tanton, L.T. (2005); Continental magmatism caused by lithospheric delamination; *Geological Society of America Special Paper* **388** p. 449-461
- Emslie, R.F. (1991); Granitoids of rapakivi granite-anorthosite and related associations; *Precambrian Research* **51** p. 173-192
- Essene, E.J., Claflin, C.L., Giorgetti, G., Mata, P.M., Peacor, D.R., Árkai, P. and Rathmell, M.A. (2005); Two-, three- and four-feldspar assemblages with hyalophane and celsian: implications for phase equilibria in BaAl₂Si₂O₈-CaAl₂Si₂O₈-NaAlSi₃O₈-KAlSi₃O₈; *European Journal of Mineralogy* **17-4** p. 515-535
- Ferry, J.M. and Watson, E.B. (2007); New thermodynamic models and revised calibrations for the Ti-inzircon and Zr-in-rutile thermometers; *Contributions to Mineralogy and Petrology* 154 p. 429-437
- Fraga, L.M., Reis, N.J., Dall'Agnol, R. and Armstrong, R. (2008); Cauarane-Coeroene belt the tectonic southern limit of the preserved rhyacian crustal domain in the Guyana shield, northern Amazonian craton; 33rd International Geological Congress (Oslo, Norway) abstract
- Fraga, L.M., Macambiro, M.J.B., Dall'Agnol, R. and Costa, J.B.S. (2009); 1.94-1.93 Ga charnockitic magmatism from the central part of the Guyana Shield, Roraima, Brazil: Single-zircon evaporation data and tectonic implications; *Journal of South American Earth Sciences* 27 p. 247-257
- Frost, B.R. and Frost, C.D. (1987); CO₂, melts and granulite metamorphism; Nature 327 p. 503-506
- Frost, B.R., Frost, C.D., Hulsebosch, T.P. and Swapp, S.M. (2000); Origin of the charnockites of the Louis Lake batholith, Wind River Range, Wyoming; *Journal of Petrology* **41-12** p.1759-1776
- Frost, B.R. and Frost, C.D. (2008); On charnockites; Gondwana Research 13 p. 30-44
- Fu, B., Page, F.Z., Cavosie, A.J., Fournelle, J., Kita, N.T., Lackey, J.S., Wilde, S.A. and Valley, J.W. (2008); Ti-in-zircon thermometry: applications and limitations; *Contributions to Mineralogy and Petrology* **156** p. 197-215
- Fuhrman, M.L. and Lindsley, D.H. (1988); Ternary-feldspar modelling and thermometry; *American Mineralogist* **73** p. 201-215
- Fulmer, E.C. and Kruijer, T. (2009); The nature of batholith formation: detailed field, geochemical and isotopic constraints on the assembly of the Sentinel Granodiorite, Sierra Nevada Batholith, USA; MSc-thesis, Vrije Universiteit Amsterdam
- Green, T.H. and Pearson, N.J. (1986); Ti-rich accessory phase saturation in hydrous mafic-felsic compositions at high P, T; *Chemical Geology* 54 p. 185-201

- Groot, K. de (2008); Geothermo(baro)metry of ultrahigh-temperature metamorphism in the Bakhuis Mountain, Surinam; MSc-thesis, Vrije Universiteit Amsterdam
- Hamilton, P.J., O'Nions, R.K., Bridgwater, D. and Nutman, A. (1983); Sm-Nd studies of Archaean metasediments and metavolcanics from West Greenland and their implications for the Earth's early history; *Earth and Planetary Science Letters* **62-2** p. 263-272
- Hanchar, J.M. and Westrenen, W. van (2007); Rare earth element behaviour in zircon-melt systems; *Elements* **3** p. 37-42
- Harley, S.L. (1998); On the occurrence and characterization of ultrahigh-temperature crustal metamorphism; *Geological Society of London Special Publication* **138** p. 81-107
- Harley, S.L. (2008); Refining the P-T records of UHT crustal metamorphism; *Journal of metamorphic Geology* **26** p. 125-154
- Harrison, T.M. and Watson, E.B. (1983); Kinetics of zircon dissolution and zirconium diffusion in granitic melts of variable water content; *Contributions to Mineralogy and Petrology* 84-1 p. 66-72
- Harrison, T.M. and Watson, E.B. (1984); The behaviour of apatite during crustal anatexis: equilibrium and kinetic considerations; *Geochimica et Cosmochimica Acta* **48** p. 1467-1477
- Harrison, T.M., Aikman, A., Holden, P., Walker, A.M., McFarlane, C., Rubatto, D. and Watson, E.B. (2005); Testing the Ti-in-zircon thermometer; American Geophysical Union, fall meeting abstract
- Harrison, T.M., Watson, E.B. and Aikman, A.B. (2007); Temperature spectra of zircon crystallization in plutonic rocks; *Geology* **35-7** p. 635-638
- Hellstrom, J., Paton, C., Woodhead, J.D. and Hergt, J.M. (2008); Iolite: software for spatially resolved LA-(quad and MC) ICPMS analysis; Mineralogical Association of Canada short course series **40** p. 343-348
- Hinton, R.W. and Upton, B.G.J. (1991); The chemistry of zircon: variations within and between large crystals from syenite and alkali basalt xenoliths; *Geochimica et Cosmochimica Acta* 55 p. 3287-3302
- Hofmann, A.E., Valley, J.W., Watson, E.B., Cavosie, A.J. and Eiler, J.M. (2009); Sub-micron scale distributions of trace elements in zircon; *Contributions to Mineralogy and Petrology* 158 p. 317-335
- Hood, P. and Tyl, I. (1973); Residual magnetic anomaly map of Guyana and its regional geological interpretation; Preprint 2nd Latin-American Geological Congress, Caracas, Venezuela
- Hokada, T. (2001); Feldspar thermometry in ultrahigh-temperature metamorphic rocks: evidence of crustal metamorphism attaining ~1100 °C in the Archean Napier Complex, East Antarctica; American Mineralogist **86** p. 932-938
- Holland, T.H. (1900); The charnockite series, a group of Archaean hypersthenic rocks in peninsular India; *Geological Survey of India Memoir* **2** p. 192-249
- Hoskin, P.W.O. and Schaltegger, U. (2003); The composition of zircon and igneous and metamorphic petrogenesis; In: Reviews in Mineralogy and Geochemistry **53** p. 27-62
- Hubbard, F.H. (1989); The geochemistry of Proterozoic lower-crustal depletion in southwest Sweden; Lithos 23 p. 101-113

- Irvine, T.N. and Baragar, W.R.A. (1971); A guide to the chemical classification of the common volcanic rocks; *Canadian Journal of Earth Sciences* **8-5** p. 523-548
- Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C. and Essling, A.M. (1971); Precision measurement of half-lives and specific activities of ²³⁵U and ²³⁸U; *Physical Review* C4 p. 1889-1906
- Kar, R., Bhattacharya, S. and Sheraton, J.W. (2003); Hornblende-dehydration melting in mafic rocks and the link between massif-type charnockite and associated granulites, Eastern Ghats Granulite Belt, India; *Contributions to Mineralogy and Petrology* 145 p. 707-729
- Kar, R. and Bhattacharya, S. (2010); New experimental constraints: implications for petrogenesis of charnockite of dioritic composition; *Natural Science* **2-10** p. 1085-1089
- Kelsey, D.E. (2008); On ultrahigh-temperature crustal metamorphism; Gondwana Research 13 p. 1-29
- Kemp, A.I.S., Hawkesworth, C.J., Foster, G.L., Paterson, B.A., Woodhead, J.D., Hergt, J.M., Gray, C.M. and Whitehouse, M.J. (2007); Magmatic and crustal differentiation history of granitic rocks from Hf-O isotopes in zircon; *Science* **315** p. 980-983
- Keppler, H. and Wyllie, P.J. (1990); Role of fluids in transport and fractionation of uranium and thorium in magmatic processes; *Nature* **348** p. 531-533
- Kilpatrick, J.A. and Ellis, D.J. (1992); C-type magmas: igneous charnockites and their extrusive equivalents; *Transactions of the Royal Society of Edinburgh: Earth Sciences* **83** p. 155-164
- Kroonenberg, S.B. (1976); Amphibolite-facies and granulite-facies metamorphism in the Coeroeni-Lucie area, southwestern Suriname; *Geologisch Mijnbouwkundige Dienst van Suriname Mededeling* **25** p. 109-289
- Kroonenberg, S.L. and Roever, E.W.F. de (2009); Geological evolution of the Amazonian Craton; in: Amazonia, landscape and species evolution; Wiley-Blackwell
- Lamarão, C.N., Dall'Agnol, R. and Pimentel, M.M. (2005); Nd isotopic composition of Paleoproterozoic volcanic and granitoid rocks of Vila Riozinho: implications for the crustal evolution of the Tapajo's gold province, Amazon Craton; *Journal of South American Earth Sciences* 18 p. 277-292
- Lee, J.K.W., Williams, I.S. and Ellis, D.J. (1997); Pb, U and Th diffusion in natural zircon; *Nature* **390** p. 159-162
- Le Maitre, R.W. (ed.) (1989); A classification of igneous rocks and glossary of terms; Blackwell Scientific Publications
- Linnen, R.L. and Keppler, H. (2002); Melt composition control of Zr/Hf fractionation in magmatic processes; *Geochimica et Cosmochimica Acta* **66** p. 3293-3301
- Lowery Claiborne, L., Miller, C.F., Walker, B.A., Wooden, J.L., Mazdab, F.K. and Bea, F. (2006); Tracking magmatic processes through Zr/Hf ratios in rocks and Hf and Ti zoning in zircons: an example from the Spirit Mountain batholith, Nevada; *Mineralogical Magazine* **70-5** p. 517-543
- Ludwig, K.R. and Silver, L.T. (1977); Lead-isotope inhomogeneity in Precambrian igneous K-feldspars; Geochimica et Cosmochimica Acta **41** p. 1457-1471
- Ludwig, K.R. (2008); Isoplot 3.6: a geochronological toolkit for Microsoft Excel; Berkeley Geochronology Center, Special Publication **4**, 78 p.

- Lugmair, G.W. and Marti, K. (1978); Lunar initial ¹⁴³Nd/¹⁴⁴Nd: differential evolution of the lunar crust and mantle; *Earth and Planetary Science Letters* **39** p. 349-357
- Mahlen, N.J., Beard, B.L., Johnson, C.M. and Lapen, T.J. (2008); An investigation of dissolution methods for Lu-Hf and Sm-Nd isotope studies in zircon- and garnet-bearing whole-rock samples; *Geochemistry Geophysics Geosystems* **9-1**
- Mattinson, J.M. (1987); U-Pb ages of zircons: a basic examination of error propagation; *Chemical Geology* **66** p. 151-162
- Mattinson, J.M. (2000); Revising the "Gold Standard" the uranium decay constants of Jaffey et. al., 1971; AGU spring meeting abstracts
- McDonough, W.F. and Sun, S.-s. (1995); The composition of the Earth; *Chemical Geology* **120** p. 223-253
- Mezger, K., Hanson, G.N. and Bohlen, S.R. (1989); U-Pb systematics of garnet: dating the growth of garnet in the Late Archean Pikwitonei granulite domain at Cauchon and Natawahunan Lakes, Manitoba, Canada; *Contributions to Mineralogy and Petrology* **101** p. 136-148
- Mezger, K. and Krogstad, E.J. (1997); Interpretation of discordant U-Pb zircon ages: an evaluation; Journal of Metamorphic Geology 15 p. 127-140
- Mikhalsky, E.V., Sheraton, J.W. and Hahne, K. (2006); Charnockite composition in relation to the tectonic evolution of East Antarctica; *Gondwana Research* **9** p. 379-397
- Milesi, J.P., Egal, E., Ledru, P., Vernhet, Y., Thiéblemont, D., Cocherie, A., Tegyey, M., Martel-Jantin, B. and Lagny, Ph. (1995); Les minéralisations du Nord de la Guyane française dans leur cadre géologique; *Chronique de la Recherche Minière, France* **518** p. 5-58
- Miller, C.F., McDowell, S.M. and Mapes, R.W. (2003); Hot and cold granites? Implications of zircon saturation temperatures and preservation of inheritance; *Geology* **31-6** p. 529-532
- Munksgaard, N.C., Thost, D.E. and Hensen, B.J. (1992); Geochemistry of Proterozoic granulites from northern Prince Charles Mountains, East Antarctica; *Antarctic Science* **4-1** p. 59-69
- Newton, R.C. (1992); An overview of charnockite; Precambrian Research 55 p. 399-405
- Patino Douce, A.E. and Beard, J.S. (1995); Dehydration melting of biotic gneiss and quartz amphibolite from 3 to 15 kbar; *Journal of Petrology* **36** p. 707-738
- Paton, C., Woodhead, J.D., Hellstrom, J.C., Hergt, J.M., Greig, A. and Maas, R. (2010); Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction; *Geochemistry Geophysics Geosystems* 11
- Pearce, J.A. and Cann, J.R. (1973); Tectonic setting of basic volcanic rocks determined using trace element analysis; *Earth and Planetary Science Letters* **19** p. 290-300
- Pearce, J.A. (1982); Trace element characteristics of lavas from destructive plate boundaries; In: Thorpe, R.S. (ed.); Andesites; Wiley p. 525-548
- Pearce, J.A., Harris, N.B.W. and Tindle, A.G. (1984); Trace element discrimination diagrams for the tectonic interpretation of granitic rocks; *Journal of Petrology* **25** p. 956-983
- Priem, H.N.A., Boelrijk, N.A.I.M., Hebeda, E.H., Verdurmen, E.A.Th. and Verschure, R.H. (1971); Isotopic ages of the Trans-Amazonian acidic magmatism and the Nickerie metamorphic episode in the Precambrian basement of Suriname, South America; *Geological Society of America Bulletin* 82 p. 1667-1680

- Priem, H.N.A., Boelrijk, N.A.I.M., Hebeda, E.H., Kroonenberg, S.L., Verdurmen, E.A.Th. and Verschure, R.H. (1977); Isotopic ages in the high-grade metamorphic Coeroeni Group, SW Suriname; *Geologie en Mijnbouw* 56 p. 155-160
- Priem, H.N.A., Boelrijk, N.A.I.M., Hebeda, E.H., Kuyper, R.P., De Roever, E.W.F., Verdurmen, E.A.Th., Verschure, R.H. and Wielens, J.B. (1978); How old are the supposedly Archaean charnockitic granulites in the Guiana Shield basement of western Suriname (South America)?; USGS Open File Report **78-701** p. 341-343
- Raczek, O., Stoll, B., Hofmann, A.W. and Jochum, K.P. (2001); High-precision trace element data for the USGS reference materials BCR-1, BCR-2, BHVO-1, BHVO-2, AGV-1, AGV-2, DTS-1, DTS-2, GSP-1 and GSP-2 by ID-TIMS and MIC-SSMS; *Geostandards Newsletter* 25-1 p. 77-86
- Rajesh, H.M. (2007); The petrogenetic characterization of intermediate and silicic charnockites in high-grade terrains: a case study from southern India; *Contributions to Mineralogy and Petrology* 154 p. 591-606
- Ranson, W.A. (1986); Complex exsolution in inverted pigeonite: exsolution mechanisms and temperatures of crystallisation and exsolution; *American Mineralogist* **71** p. 1322-1336
- Rasband, W.S. (1997); ImageJ, U.S. National Institutes of Health, Bethesda, Maryland, USA; http://imagej.nih.gov/ij/
- Reis, N.J., Faria, M.S.G. de, Fraga, L.M. and Haddad, R.C. (2000); Orosirian calc-alkaline volcanism and the Orocaima event in the northern Amazonian craton, eastern Roraima state, Brazil; *Revista Brasileira de Geosciências* **30-3** p. 380-383
- Robertson, J.K. and Wyllie, P.J. (1971); Experimental studies on rocks from the Deboullie Stock, northern Maine, including melting relations in the water-deficient environment; *Journal of Geology* **79-5** p. 549-571
- Roever, E.W.F. de (1975a); Provisional lithologic framework of the Falawatra Group, W. Suriname; *Geologisch Mijnbouwkundige Dienst van Suriname Mededeling* **23** p. 34-45
- Roever, E.W.F. de (1975b); Geology of the central part of the Bakhuis mountains (W Suriname); Geologisch Mijnbouwkundige Dienst van Suriname Mededeling **23** p. 65-101
- Roever, E.W.F. de, Lafon, J.M., Delor, C., Cocherie, A., Rossi, P., Guerrot, C. and Potrel, A. (2003);
 The Bakhuis ultrahigh-temperature granulite belt (Suriname): I. petrological and geochronological evidence for a counterclockwise P-T path at 2.07-2.05 Ga; *Géologie de la France* 2-3-4 p. 175-205
- Roever, E.W.F. de, Lafon, J.M., Delor, C. and Guerrot, C. (2010); Orosirian magmatism and metamorphism in Surinam: new geochronological constraints; 45° Congresso Brasileiro de Geologia, Belem *(poster)*
- Rollinson, H.R. (1993); Using geochemical data: evaluation, presentation, interpretation; Pearson Prentice Hall, 352 p.
- Rosa Costa, L.T., Ricci, P.S.F., Lafon, J.M., Vasquez, M.L., Carvalho, J.M.A., Klein, E.L. and Macambira, E.M.B. (2003); Geology and geochronology of Archean and Paleoproterozoic domainsof Southwester Amapá and northwestern Pará, Brazil, southeastern Guiana shield; *Géologie de la France* 2-3-4 p. 101-120
- Rudnick, R.L. and Presper, T. (1990); Geochemistry of intermediate/- to high-pressure granulites; In: Vielzeuf, D. and Vidal, P. (eds.); Granulites and crustal evolution; Kluwer Academic Publishers p. 523-550

- Santos, J.O.S., Potter, P.E., Reis, N.J., Hartmann, L.A., Fletcher, I.R. and McNaughton, N.J. (2003); Age, source, and regional stratigraphy of the Roraima Supergroup and Roraima-like outliers in northern South America based on U-Pb geochronology; *Geological Society of America Bulletin* 115-3 p. 331-348
- Santos, J.O.S., Breemen, O.B. van, Groves, D.I., Hartmann, L.A., Almeida, M.E., McNaughton, N.J. and Fletcher, I.R. (2004); Timing and evolution of multiple Paleoproterozoic magmatic arcs in the Tapajós Domain, Amazon Craton: constraints from SHRIMP and TIMS zircon, baddeleyite and titanite U-Pb geochronology; *Precambrian Research* 131 p. 73-109
- Santosh, M. and Omori, S. (2008); CO₂ flushing: a plate tectonic perspective; *Gondwana Research* **13-1** p. 86-102
- Santosh, M., Kusky, T. and Wang, L. (2011); Supercontinent cycles, extreme metamorphic processes, and changing fluid regimes; *International Geology Review (in press)*
- Schoene, B. and Bowring, S.A. (2006); U-Pb systematics of the McClure Mountain syenite: thermochronological constraints on the age of the ⁴⁰Ar/³⁹Ar standard MMhb; *Contributions to Mineralogy and Petrology* **151** p. 615-630
- Schoene, B., Crowley, J.L., Condon, D.J., Schmitz, M.D. and Bowring, S.A. (2006); Reassessing the uranium decay constants for geochronology using ID-TIMS U-Pb data; *Geochimica et Cosmochimica Acta* 70 p. 426-445
- Shannon, R.D. (1976); Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides; *Acta Crystallographica* A32 p. 751-767
- Sheraton, J.W. and Black, L.P. (1988); Chemical evolution of granitic rocks in the East Antarctic Shield, with particular reference to post-orogenic granites; *Lithos* **21** p. 37-52
- Sheraton, J.W., Black, L.P. and Tindle, A.G. (1992); Petrogenesis of plutonic rocks in a Proterozoic granulite-facies terrane the Bunger Hills, East Antarctica; *Chemical Geology* **97** p. 163-198
- Springer, W. and Seck, H.A. (1997); Partial fusion of basic granulite at 5 to 15 kbar: implications for the origin of TTG magmas; *Contributions to Mineralogy and Petrology* **127** p. 30-45
- Stacey, J.S. and Kramers, J.D. (1975); Approximation of terrestrial lead isotope evolution by a two-stage model; *Earth and Planetary Science Letters* **26-2** p. 207-221
- Steiger, R.H. and Jäger, E. (1977); Subcommission on geochronology: convention on the use of decay constants in geo- and cosmochronology; *Earth and Planetary Science Letters* **36** p. 359-362
- Štípská, P. and Powell, R. (2005); Does ternary feldspar constrain the metamorphic conditions of highgrade meta-igneous rocks? Evidence from orthopyroxene granulites, Bohemian Massif; *Journal* of Metamorphic Geology 23-8 p. 627-647
- Streckeisen, A. (1976); To each plutonic rock its proper name; Earth Science Reviews 12 p. 1-33
- Sun, S.-s. and McDonough, W.F. (1989); Chemical and isotopic systematics of oceanic basalts: implications for mantle composition and processes; *Geological Society, London, Special Publications* 42 p. 313-345
- Tassinari, C.C.G., Munhá, J.M.U., Teixeira, W., Nutman, A., Palácios, T., Sosa, S.C. and Calado, B.O. (2003); Thermochronological history of the Imataca complex, NW Amazonian Craton; 4th South American Symposium on Isotope Geology short papers 1 p. 121-123
- Thirlwall, M.F. (1991); Long-term reproducibility of multicollector Sr and Nd isotope ratio analysis; *Chemical Geology* **94**, p. 85-104

- Wang, Q., Wyman, D.A., Xu, J., Jian, P., Zhao, Z., Li, C., Ma, J. and He, B. (2007); Early Cretaceous adakites in the Northern Dabie Complex, central China: implications for partial melting and delamination of thickened lower crust; *Geochimica et Cosmochimica Acta* 71-10 p. 2609-2636
- Wark, D.A. and Watson, E.B. (2006); TitaniQ: a titanium-in-quartz geothermometer; *Contributions to Mineralogy and Petrology* **152** p. 743-754
- Watson, E.B. and Harrison, T.M. (1983); Zircon saturation revisited: temperature and composition effects in a variety of crustal magma types; *Earth and Planetary Science Letters* **64** p. 295-304
- Watson, E.B., Wark, D.A. and Thomas, J.B. (2006); Crystallisation thermometers for zircon and rutile; *Contributions to Mineralogy and Petrology* **151** p. 413-433
- Weis, D., Kieffer, B., Maerschalk, C., Barling, J., Jong, J. de, Williams, G.A., Hanano, D., Pretorius, W., Mattielli, N., Scoates, J.S., Goolaerts, A., Friedman, R.M. and Mahoney, J.B. (2006); Highprecision isotopic characterization of USGS reference materials by TIMS and MC-ICP-MS; *Geochemistry Geophysics Geosystems* 7-8
- Wells, P.R.A. (1980); Thermal models for the magmatic accretion and subsequent metamorphism of continental crust; *Earth and Planetary Science Letters* **46** p. 253-265
- Wen, S. and Nekvasil, H. (1994); SOLVCALC: an interactive graphics program package for calculating the ternary feldspar solvus for two-feldspar geothermometry; *Computers & Geosciences* 20-6 p. 1025-1040
- Wetherill, G.W. (1956); Discordant uranium-lead ages; *Transactions of the American Geophysical Union* **37-3** p. 320-326
- Wiedenbeck, M., Hanchar, J.M., Peck, W.H., Sylvester, P., Valley, J., Whitehouse, M., Kronz, A., Morishita, Y., Nasdala, L., Fiebig, J., Franchi, I., Girard, J.P., Greenwood, R.C., Hinton, R., Kita, N., Mason, P.R.D., Norman, M., Ogasawara, M., Piccoli, P.M., Rhede, D., Satoh, H., Schulz-Dobrick, B., Skår, Ø., Spicuzza, M.J., Terada, K., Tindle, A., Togashi, S., Vennemann, T., Xie, Q. and Zheng, Y.F. (2004); Further characterisation of the 91500 Zircon crystal; *Geostandards and Geoanalytical Research* 28-1 p. 9-39
- Williams, L.S., Compston, W., Black, L.P., Ireland, T.R. and Foster, J.J. (1984); Unsupported radiogenic Pb in zircon: a cause of anomalously high Pb-Pb, U-Pb and Th-Pb ages; *Contributions to Mineralogy and Petrology* 88 p. 322-327
- Winter, J.D. (2001); An introduction to igneous and metamorphic petrology; Prentice Hall, 697 p.
- Yacobi, B.G. and Holt, D.B. (1990); Cathodoluminescence microscopy of inorganic solids; New York, Plenum
- Young, D.N., Zhao, J.X., Ellis, D.J. and McCulloch, M.T. (1997); Geochemical and Sr-Nd isotopic mapping of source provinces for the Mawson charnockites, east Antarctica: implications for Proterozoic tectonics and Gondwana reconstruction; *Precambrian Research* 86 p. 1-19
- Yuan, H., Gao, S., Liu, X., Li, H., Günther, D. and Wu, F. (2004); Accurate U-Pb age and trace element determinations of zircon by laser ablation-inductively coupled plasma-mass spectrometry; *Geostandards and Geoanalytical Research* 28-3 p. 353-370
- Zhao, G., Cawood, P.A., Wilde, S.A. and Sun, M. (2002); Review of global 2.1-1.8 Ga orogens: implications for a pre-Rodinia supercontinent; *Earth-Science Reviews* **59** p. 125-162
- Zhao, J.X., Ellis, D.J., Kilpatrick, J.A. and McCulloch, M.T. (1997); Geochemical and Sr-Nd isotopic study of charnockites and related rocks in the northern Prince Charles Mountains, East Antarctica: implications for charnockite petrogenesis and proterozoic crustal evolution; *Precambrian Research* 81 p. 37-66