The Regional Extent of Ultrahigh-temperature Metamorphism in the Bakhuis Granulite Belt, W Surinam

- a feldspar thermometric study



J.A.M. Nanne

Master Thesis Solid Earth

Supervised by:

Dr. E.W.F. de Roever

Dr. F.M. Brouwer



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Figure on front page: A photograph of a petrographic thin section in crossed polarised light with gypsum plate. The centre of the figure shows a mesoperthite of ~4mm from sample FN45A, Vanamkreek, Bakhuis Granulite Belt, W Surinam.

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Faculty of Earth and Life Sciences Petrology Department VU University, Amsterdam

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ABSTRACT

The Bakhuis Granulite Belt (BGB) in the largest Proterozoic granulite-facies domain in northern South America. A metapelite area of 50-100 km^2 in the NE of the belt shows orthopyroxene + sillimanite + quartz \pm sapphirine with 8-10wt% Al₂O₃ in the orthopyroxene, characteristic for ultrahigh-temperature (UHT) metamorphism. Evidence for UHT metamorphism in pelitic gneisses elsewhere in the belt is very rare and may have disappeared due to widespread retrograde metamorphism and deformation. Ternary feldspar thermometry was used to determine the extent of UHT metamorphism in the belt. Metapelite and granulite samples with exsolved feldspar, mesoperthite or antiperthite, were selected for one-feldspar thermometry. Based on electron microprobe analysis and image analysis the original feldspar composition was calculated, from which the solvus temperature has been determined using the feldspar model of Fuhrman & Lindsley (1988). The selected samples from 15 locations spread over the BGB showed metamorphic temperatures from 901°C to 1047°C, above the 900°C minimum temperature of UHT metamorphism. This indicates that the entire BGB, 3000 km², has witnessed UHT metamorphism. Additional metapelite samples showed the rare presence of Al-rich orthopyroxene and, in one case, of sapphirine in a quartz-rich rock, confirming the regional extent of UHT metamorphism. UHT assemblages in the metapelitic rocks show a regional variation, with characteristic opx + sil + qz and spr+ qz in the NE area, and atypical UHT assemblage $crd + sil \pm (Al-rich)$ opx elsewhere in the belt. The UHT character of the latter assemblage is indicated by the relatively rare presence of Al-rich opx and by the temperature obtained from feldspar thermometry.

Opaque Fe-Ti oxides in the metapelitic rocks were identified as pure magnetite + Ti-hematite, from which the oxygen fugacity during UHT metamorphism could be estimated to range from approximately 10^{-11} to 10^{-6} MPa. Further evidence of a high fO_2 is the incorporation of Fe³⁺ in orthopyroxene, sillimanite, sapphirine and corundum. The absence of coeval garnet from the UHT assemblages probably is caused by the high fO_2 . In the absence of garnet geobarometry is difficult. Despite the strong oxidation the incorporation of Fe³⁺ in orthopyroxene is low, allowing geothermobarometry on Al-rich orthopyroxene alone. A pressure of 9½ kbar and temperatures in the order of 50°C lower than feldspar temperatures were obtained. The pressure is slightly higher than the 8½ kbar suggested by de Roever et al. (2003). Modelling is required to validate this preliminary result.

By LA-ICP-MS zircons of three samples from the SW part of the BGB were dated. A pelitic gneiss yields a metamorphic age of 2,073 Ma, coinciding with the age of UHT metamorphism in the NE and central part of the BGB (de Roever et al., 2003). This indicates that the BGB witnessed a single UHT event. Zircons from a sillimanite-cordierite granodiorite showed a complex growth history, with three populations of estimated ages of 2.13 Ga, 2.07 Ga and 1.99 Ga. Geochemical data and the presence of Alrich silicates point to an S-type granite, most likely derived by partial melting from pelitic rocks metamorphosed during the UHT event at 2.07 Ga. The youngest age of 1.99 Ga closely corresponds to the 1.98 Ga age of widespread charnockites in the SW of the BGB (Klaver, 2011). The S-type granite magma apparently did not mix with the magma of charnockites nearby. The oldest zircon population, 2.13 Ga, represents inherited detrital zircon which is also found in the pelitic gneiss. Zircons from a mesoperthite granulite layer defined an age of 2,04 Ga, slightly younger than the UHT event. Based on geochemical data this rock type is interpreted as representing a K-rich, granitic melt extracted from associated granulites during or just before the UHT metamorphic event. The slightly younger age might be explained by crystallisation upon cooling after UHT metamorphism. The extraction of granitic melt suggests that the associated granulites are restitic and that their potassium-poor signature is not derived from K-poor precursors.

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1. INTRODUCTION

1.1 Scope of this Study

1.1.1 Introduction

The subject of this thesis is Ultrahigh-Temperature (UHT) metamorphism in the Bakhuis Mountains, located in the western part of Suriname, South America. The central part of the Bakhuis Mountains is formed by the Bakhuis Granulite Belt (BGB), an elongated belt of more than 3000km². De Roever (1973, 1975) recognised the exceptionally high-grade character of the granulites in the BGB, with sapphirine and aluminous orthopyroxene + sillimanite. These minerals are now known to be characteristic of UHT metamorphism (e.g., Harley, 1998a, 2008). They occur in a metapelitic area in the northeast, the 'Fallawatra occurrence', of the BGB (de Roever et al., 2003; de Groot, 2008). This area is comparatively small, $50 - 100 \text{ km}^2$, and is surrounded by intermediate and mafic granulites that do not show evidence of UHT metamorphism. That lack of evidence is, however, common for UHT metamorphism elsewhere in the world as characteristic minerals occur mainly in metapelitic rocks. Other metapelite intercalations in the BGB differ considerably in mineralogy from the Fallawatra occurrence, the orthopyroxene + sillimanite assemblage is rare and sapphirine very rare. Metapelitic rocks in these areas show widespread and intense recrystallisation due to retrogressive metamorphism and deformation. In addition, locally strong mylonitisation is shown. This may have largely wiped out evidence for UHT metamorphism in the other metapelite areas. Although these factors appear to be important, other factors may also have played a role. Coarse cordierite is a common constituent of the metapelites in the other areas, which is less common for UHT metamorphism. However, the rare occurrence of orthopyroxene together with sillimanite in these other metapelite areas would suggest a UHT-like metamorphism or a transition to UHT metamorphism.

1.1.2 Aim of this study

UHT metamorphism has been defined as a type of granulite-facies metamorphism at $T > 900^{\circ}C$ (Harley, 1998a). The main aim of this project is to determine whether the entire Bakhuis Granulite Belt witnessed UHT metamorphic conditions, with peak temperatures exceeding 900°C over an area of more than 3,000km², or that UHT conditions have been attained only locally, in the Fallawatra occurrence. Another goal of this project is to better establish the age of UHT metamorphism in the belt. Klaver (2011) indicated a younger, ultrahigh-temperature event in the SW of the belt, implying that UHT metamorphism might have occurred at different time in different parts of the belt. Pb-Pb and U-Pb zircon ages of high-grade metamorphism have been determined for metapelitic rocks in the centre and NE of the belt (de Roever et al., 2003), but geochronological data are missing in the SW. As the main aim of this research is to provide evidence that the whole Bakhuis belt experienced UHT metamorphism, it should first of all be determined whether the metamorphic rocks were formed during a single event or in different time periods. In addition, preliminary work on two rather extraordinary rock types, a mesoperthite granulite and a sillimanite-cordierite granodiorite, will be performed. The goal is to put these two rock types within a time and compositional framework within the BGB. Overall, this thesis is aiming to contribute to a better understanding of the geological history of the Bakhuis Granulite Belt.

1.2 Approach

Geothermometry appears to be the best method to evaluate the regional extent of UHT metamorphism in the BGB. The alumina content of orthopyroxene is a robust geothermometer, but orthopyroxene is too rare in most BGB metapelitic areas to be practical. A much better tool might be ternary feldspar thermometry. Mesoperthite has been found at many locations in metapelitic rocks and antiperthite is

common in both pelitic gneisses and felsic granulites. Furthermore, a thermometer such as Ti-in-Q might also be very useful because of the abundance of quartz in felsic rock types.

Thermodynamic modelling may contribute greatly to quantification of the metamorphic conditions of the BGB. De Groot (2008) established peak temperatures of metamorphism through thermometry, but pressure determination failed. Thermodynamic modelling might establish the pressure required for the orthopyroxene + sillimanite assemblage and might also provide an explanation for the rarity of garnet. Due to time constraints it was not possible to incorporate the latter approach within this study.

To establish whether UHT metamorphism in the SW of the BGB occurred in the same time period as determined for the central and NE part, age determinations will be carried out on a pelitic gneiss from an occurrence in the south-western part of the belt. In order to establish whether thermometric data from other rock types than metapelite can be used to determine the extent of UHT metamorphism. Exploratory zircon dating and XRF whole rock analysis will be carried out on a single sample of mesoperthite granulite and of sillimanite-cordierite granodiorite.

1.3 Project Framework

This research project was carried out as part of the curriculum of the MSc-program Earth Sciences – Solid Earth at VU University Amsterdam and constitutes the Master Thesis Solid Earth (course code 450199), which is valid for 27 ECTS and in this case combined with an extension of 12 ECTS. The purpose of this course is to design, execute and document scientific research. The project was supervised by Dr. Emond W.F. de Roever, guest lecturer at the VU University Amsterdam and formerly employed as exploration geologist at the Geological and Mining Survey of Suriname (GMD), and Dr. Fraukje M. Brouwer, senior lecturer at VU University Amsterdam. Sample processing and analysis were all carried out at the Faculty of Earth and Life Sciences of the VU University Amsterdam, except for the Laser Ablation ICP-MS analysis which were executed at the Faculty of Geosciences at the University Utrecht.

The project was financially supported by the Stichting Dr. Schürmann Fonds, the Stichting Molengraaff Fonds, and the Faculty of Earth and Life Sciences of the VU University Amsterdam. The Geological and Mining Service (GMD), Surinam, provided samples. The head of the GMD, M. Autar, provided technical support.

1.4 Project Outline

Chapter 2, 3 and 4 of this thesis are introductory, providing background information on UHTmetamorphism, the geological setting, and thermo(baro)metry, respectively. Methods applied in this study are outlined in Chapter 5. Chapter 6 contains a description of the field observations and petrography of the collected rock samples followed by Chapter 7 which reports the analytical results. Chapter 8 comprises a discussion of all the results. Finally, Chapter 9 presents the main conclusions of this study, and suggestions for future research. Mineral abbreviations follow Whitney & Evans (2010).

2. ULTRAHIGH-TEMPERATURE METAMORPHISM

2.1 Definition

Ultrahigh-temperature (UHT) metamorphism is defined as crustal metamorphism that occurred at peak temperatures in excess of 900°C, at only moderate pressures (7-13 kbar) and on a regional scale, >1000 km² (Fig. 2.1; Harley, 1989, 1998a; Brown, 2006). Moderate pressures correspond to mid- to deep-crustal levels, about 20-40 km deep. The high temperature implies a geothermal gradient of >20°C/km. UHT metamorphism is considered a subdivision of the granulite facies, which is generally regarded to encompass metamorphic conditions of 3-15 kbar and 700-1000°C (Harley, 1989, 1992).

The acceptance of UHT metamorphism as a common type of metamorphism was slow. This was in part because diagnostic assemblages (section 2.2) occur mainly in Mg-Al rich lithologies that are volumetrically rare in nature (Kelsey, 2008) and in part because many geothermometers used at that time showed lower temperatures due to resetting. Until the mid-1990s, most petrologists believed that regional metamorphism rarely took place at temperatures exceeding 850°C. Domains that showed higher temperatures were considered to be insignificant and anomalous. It was mainly because of Harley's studies (Harley, 1998a,b,c) that UHT metamorphism is now generally accepted. Harley (1998a,b,c) compiled a dataset of granulite localities and demonstrated that many granulite terranes experienced temperatures above 900°C on the basis of the preserved mineral assemblages, using refined P-T

estimates. In the last decades the pressuretemperature domain of metamorphism has been greatly expanded as the extremes of metamorphism become have increasingly recognised in the geological record and techniques to constrain the extremes have greatly improved (e.g., Harley, 1998a, 2004; Pattison et al., 2003; Kelsey et al., 2003, 2005).

The recognition of UHT metamorphism has important implications for numerical models of crustal evolution because the generally assumed thermal conditions are greatly exceeded. Accurate quantitative P-T and P-T-time path records for UHT terranes provide fundamental constraints to rheological models for high-grade gneiss terranes (e.g., Harley, 1989, 1992; Sandiford & Powell, 1990, 1991; Lund et al., 2006).



Figure 2.1 Ultrahigh-temperature (UHT) metamorphism defined in pressure–temperature (P–T) space. *From Kelsey (2008)*.

2.2 Key Indicators

UHT metamorphism may be recognised by a range of diagnostic assemblages and indicators (Harley, 1998a; Kelsey et al., 2003; Kelsey, 2008; Harley, 2008). It is important to realise that mineral assemblages might have a larger stability field if Fe^{3+} and/or minor elements are incorporated into the minerals. This means that the occurrence of certain mineral assemblages alone cannot be put forward as diagnostic evidence for UHT metamorphism, but can only be considered as indicative.

Diagnostic assemblages:

1) The stable coexistence of **sapphirine** and **quartz** (Fig. 2.2a) in a reduced setting (Harley, 1998a, 2004; Kelsey et al., 2004, 2005; Kelsey, 2008; Harley, 2008).

- 2) The stable coexistence of **aluminous orthopyroxene + sillimanite** (Fig. 2.2b) in a reduced setting (Harley, 1998a, 2008; White et al., 2001; Kelsey et al., 2004).
- 3) Assemblages involving **osumilite** in association with garnet, orthopyroxene + sillimanite, or sapphirine + orthopyroxene + quartz (Carrington & Harley, 1995; Harley, 2008).
- Aluminous (>8 wt%) orthopyroxene coexisting with aluminous minerals such as sillimanite, garnet, sapphirine, and cordierite, in a reduced setting (Hensen & Harley, 1990; Harley, 1998a, 2008; Kelsey et al., 2003).

Indicative mineral assemblages:

- 5) The assemblage **spinel + quartz** (Hensen & Harley, 1990; Waters, 1991; Harley, 1998a, 2008) occurs both in UHT metamorphic rocks and granulite-facies rocks (Harley, 2008). The presence of substantial Fe³⁺, Zn and Cr in spinel may lead to an extended stability field.
- 6) The corundum + quartz assemblage is more commonly found in UHT metamorphic rocks but has also been reported in some cases for lower-grade rocks (Kelsey, 2008). The corundum in contact with quartz should not have formed from the breakdown of high-T spinel solid solutions (Harley, 2008).
- 7) **Ternary feldspar**, with mesoperthite as best candidate (Fig. 2.2c), in non-magmatic protoliths (Hokada, 2001; Štípská & Powell, 2005).
- 8) **Inverted pigeonite** and quadrilateral pyroxene (Harley, 1987, 1998a; Tsunogae et al., 2002; Fonarev et al., 2006) in non-magmatic protoliths such as ironstones.

Diagnostic assemblages are not common in nature as they occur in a restricted range of lithologies, mainly Mg-rich pelitic gneiss. Therefore, it is difficult to prove that UHT metamorphism took place in common lithologies, such as mafic granulites. However, aluminous orthopyroxene + garnet may occur not only in metapelites and metapsammites, but also in mafic granulites (Kelsey, 2008).

2.3 Distribution

Over the past 15 years, the number of areas that are inferred to have experienced UHT metamorphism has more than doubled. Until 2008, over 40 areas have been identified (Fig. 2.3; Harley, 1998a; Brown, 2006, 2007; Kelsey, 2008). Since then the number of UHT localities has continued to rise (e.g., Shimizu et al., 2009; Cutts et al., 2011; Morgunova & Perchuk, 2011; Altenberger et al., 2012; Belyanin et al., 2012; Ague et al., 2013) as more remote regions are geologically explored and as methods to diagnose UHT



Figure 2.2 Diagnostic and indicative UHT assemblages **a**. Photomicrograph (parallel nicols) of UHT granulite from Tuguiwula showing sapphirine (Spr) + quartz (Qtz) assemblage. PI—plagioclase. *From Santosh et al. (2008).* **b**. Photomicrograph of Tuguiwula UHT granulite (parallel nicols) showing the assemblage of orthopyroxene (Opx), sillimanite (Sil), quartz (Qtz), sapphirine (Spr), spinel (Spl) and garnet (Grt). *From Zhai & Santos (2011).* **c**. Back-scattered electron image of Bakhuis Granulite Belt sillimanite gneiss showing ternary feldspar (Msp - mesoperthite; sample SA714, this study).

metamorphism become more sophisticated. However, it is also possible that a number of areas have been considered as UHT on the basis of mineral assemblages that are not truly diagnostic.

UHT domains are recorded on every continent (Fig. 2.3) and occur within ancient cratons (e.g., Antarctica, Algeria, Siberia) as well as in more recent mobile belts (i.e., latest Neoproterozoic to Early Palaeozoic), but younger domains are rare. Brown (2006, 2007) investigated the temporal distribution of UHT localities throughout Earth's history. He observed that granulite-facies metamorphism, including UHT metamorphism, is predominantly a Proterozoic phenomenon coinciding with the supercontinent formation cycle (Fig. 2.4). This suggests a potential causal relationship between crustal aggregation into supercontinents and increased geothermal gradients (Brown, 2006, 2007; Santosh & Omori, 2008).

2.4 Tectonic Setting

UHT metamorphism is the most thermally extreme type of crustal metamorphism, showing that crustal rocks may be subjected to temperatures exceeding 900°C without complete melting. The absence of complete melting at such high temperatures appears unlikely in the presence of water. However, if the activity of water is suppressed by the abundance of e.g., CO₂ the rock solidus shifts to significantly higher temperatures. This means that crustal rocks can withstand melting above 900°C. A hitherto unresolved problem of UHT metamorphism is its tectonic setting and heat source. Conventional collision models cannot simulate ultrahigh temperatures (Bohlen, 1991; Collins, 2002), neither has thermotectonic modelling been able to achieve temperatures above 900°C at relatively shallow depths (30-50 km). Even elevated crustal heat production cannot account for the anomalously high geothermal gradient (Kelsey, 2008). Only the keels of thickened orogenic belts might just reach these temperatures, but the pressure would then be higher than observed for UHT metamorphism.

One of the commonly invoked tectonic settings for UHT metamorphism is the back-arc of an active accretionary–extensional margin (e.g., Collins, 2002; Brown, 2006, 2007). A back-arc basin might provide a sufficient high geothermal gradient. Typical compressional textures that are common in granulite terranes can be explained to have formed during pauses in slab retreat induced by the subduction of oceanic plateaus or seamounts (Collins, 2002). Another model proposed for UHT metamorphism is an extension-magmatic accretion model, involving magmatic underplating by voluminous mafic magmas (Wells, 1980; Harley et al., 1990; Bohlen, 1991; Sajeev & Osanai, 2004). A mantle-derived thermal perturbation that brings in juvenile, hot mafic magma would be able to produce high temperatures at mid-to lower crustal levels. Recently, Santosh et al. (2011) proposed a model of ridge subduction. Subduction of a mid-oceanic ridge would give rise to a slab window that is necessarily filled with upwelling mantle material. Thus, the slab window would place hot anhydrous asthenospheric mantle against the base of the



1750 Gradient °C/GPa -1500 -1250 -750 500 500 1000 1500 2000 2500 300

Figure 2.3 Worldwide distribution of ultrahightemperature metamorphic terranes. *From Kelsey* (2008).

Figure 2.4 The age distribution of granulite-facies metamorphism, including UHT metamorphism, since the Neoarchaean. For each locality, the approximate geothermal gradient is given in °C/GPa and °C/km. *From Kelsey (2008), adapted from Brown (2006).*

overriding plate in a region that would normally be cooled and hydrated by the slab. This will then lead to a belt of UHT metamorphic rocks at deep levels of the arc and fore arc, where hydrous fluids are absent and CO_2 dominates. Another environment that seems capable of providing the required UHT conditions is post-collisional slab break-off and delamination (Harley, 2008). Even more models have been proposed (see Guo et al., 2012). The models mentioned above do not agree well with the apparent relation to the supercontinent cycle. It seems unlikely that all known UHT occurrences (Fig. 2.3) can be related to one single type of tectonic setting. This is also suggested by the occurrence of both clockwise and anticlockwise P-T-t-paths in UHT metamorphism.

3. GEOLOGICAL SETTING

3.1 Guiana Shield

3.1.1 Geological history

Almost a fourth of South America is occupied by the Amazonian Craton. With an area of $1.5 \cdot 10^6$ km² it is one of the largest cratonic areas in the world (Delor et al., 2003). The northern part of the craton is known as the Guiana Shield and the southern part as the Guaporé or Brazil Central Shield, with the Amazon trough in between (Fig. 3.1). The Guiana Shield extends from eastern Colombia, Venezuela and northern Brazil through Guyana, Surinam and French Guiana to northeastern Brazil. The present-day morphological appearance and structural and lithological features of the Guiana Shield are highly diverse (Fig. 3.2) due to a complex history of geological events



Figure 3.1 Location map of the Amazonian Craton. From da Rosa-Costa et al. (2006).

(Fig. 3.3; Delor et al., 2003). A short review of the history of the Guiana Shield will be presented here. In sub-section 3.1.2 extra attention will be paid to the granulite domains, and a specific part is contributed to the Bakhuis Granulite Belt (hereafter named BGB; section 3.3). For a more detailed description the reader is referred to Delor et al. (2003), Kroonenberg and de Roever (2009) and references therein.

Archaean rocks in the Guiana Shield are found at its north-western border, the Imataca Complex in Venezuela, and at its eastern boundary, the Amapá Block in south Amapá in Brazil. The Imataca Complex has been dated at 3.7-2.6 Ga (e.g., Montgomery and Hurley, 1978; Tassinari et al., 2004), and the large Amapá Block at 3.3-2.6 Ga (e.g., Avelar et al., 2003; Klein et al., 2003; da Rosa-Costa et al., 2006, 2008). The evolution of most of the Guiana Shield occurred during the Trans-Amazonian Orogeny from about 2.25 Ga to about 1.95 Ga (Hurley et al., 1967). The orogenic activity is related to the interaction of a West African Archaean Shield in the north and an Amazonian Archaean Shield to the south, resulting in the formation of, amongst others, an extensive greenstone belt in between. The northern part of the Guiana Shield is dominated by this Paleoproterozoic greenstone belt, extending for 1500 km along the coast (Fig. 3.2). The belt is not continuous but consists of two main parts that are separated by the BGB: the Venezuela-Guyana belt in the west and the Surinam-French-Guiana-Brazil part to the east.

Delor et al. (2003) described the orogeny in detail and divided it into two stages: the Main Transamazonian Event (2.26-2.08 Ga) and the Late Transamazonian Event (2.07-1.93 Ga). During an initial stage of the Main Transamazonian Event oceanic crust was produced in the form of juvenile tholeiitic melts with zircon ages as old as 2.22-2.21 Ga. These melts are a result of drifting apart of the Amazonian Archaean Shield and the West African Archaean Shield (Fig. 3.3a). In the next stage (Fig. 3.3b), N-S convergence of the Shields accompanied by southward subduction led to volcanism and sedimentation in the greenstone belt as well as arc volcanism that formed tonalitic-trondhjemitic-granodioritic (TTG) suites that are closely associated with the greenstones. Radiometric dating has shown that the TTG-greenstone belt was formed between 2.18 Ga and 2.13 Ga. Positive $\varepsilon_{(Nd)t}$ values (Lafrance et al., 1999; Delor et al., 2001; Nogueira et al., 2000) preclude the involvement of significant pre-Transamazonian crust (Delor et al., 2003), implying that the greenstone belt consists of juvenile material. At the end of the Main Transamazonian Event, approximately 2.1 Ga, the island-arc basins were closed so



Figure 3.2 Structural sketch map of the Guiana shield with geological legend. *From Delor et al. (2003).* Added to the map: AVP – Acid Volcano-Plutonic suite; AB – Amapá Block; BGB – Bakhuis Granulite Belt; GB – Greenstone Belt; IC – Imataca Complex; TGT – Tonalitic-Trondhjemitic-Granodioritic suite.



that further compression led to sinistral displacement of the Amazonian and African Shields (Fig. 3.3c). During this stage of this event, pull-apart basins were formed and a suite of granitoid rocks was produced which covers a large part of southern French Guiana and south-eastern Surinam and was dated at 2.11-2.08 Ga (Delor et al., 2003). Between 2.07 Ga and 2.05 Ga continued sinistral shear led to crustal stretching and intense deformation of the TTG-greenstone belt and the granitic suite (Fig. 3.3d). The crustal stretching led to shield-scale boudinage, a huge 'pinch and swell' structure" with two E-W oriented TTG-Greenstone boudins between which the BGB was formed (Fig. 3.2). As graphically displayed in Figure 3.3d, the TTG-greenstone belt is cross-cut by the BGB in the centre. Delor et al. (2003) argue that UHT metamorphism of the BGB is the direct result of crustal stretching between the boudins, as this led to upwelling of hot mantle material.



Figure 3.3 A geodynamic evolution model for the Paleoproterozoic terranes of the Guiana Shield. *From Delor et al.* (2003). **a.** *Eorhyacian oceanic stage (2.26-2.20 Ga).* Divergence between the Amazonian Archaean Shield and the West African Archaean Shield. **b.** Mesorhyacian arc (2.18-2.13 Ga). N-S convergence of the shields accompanied by southward subduction. **c.** Neorhyacian sinistral sliding (2.11-2.08 Ga). Closure of the island-arc basins, leading to sinistral displacement of the Amazonian and African shields. **d.** Neorhyacian crustal stretching (2.07-2.05 Ga). Continued sinistral shear led to crustal stretching and intense deformation of the TTG-greenstone belt.

Younger Late-Transamazonian high-grade metamorphism and magmatism are also recorded. The medium- to high-grade Cauarane-Coeroeni metamorphic belt occurs south of the TTG-greenstone belt. Metamorphism within this belt was in the amphibolite and granulite facies and has an age of 2.01-1.99 Ga (Fraga, 2008, 2009; de Roever et al., 2010). At approximately 1.99-1.97 Ga, a long acid volcano-plutonic belt was formed between the greenstone belt and Cauarane-Coeroeni belt (Santos et al., 2004; de Roever et al., 2010). Both belts contain a similar regional curving trend (Fig. 3.2). The acid metavolcanics show open folding, compared to intense folding of the greenstone and Cauarane-Coeroeni belts. The end of the Trans-Amazonian orogeny was marked by deposition of a thick sedimentary sequence, the Roraima Supergroup, on top of the basement, starting at or before 1,875 Ma (Santos et al., 2003). Spectacular table mountains of these sandstones and conglomerates occur in Venezuela, Guyana and NW Brazil. After the Transamazonian orogeny only local magmatic and metamorphic events were recorded in the Guiana Shield. During the Mesoproterozoic significant anorogenic acid magmatism, including typical rapakivi and tin granites, occurred in the far west and south of the Guiana Shield, and locally in areas in between (e.g., Dall'Agnol et al., 1999; Fraga, 2002). Around 1,200±100 Ma the Nickerie Tectonometamorphic Episode took place in the western part of the Guiana Shield (Priem et al., 1971). This tectonometamorphic event resulted in resetting of Rb-Sr and K-Ar mica ages in western Surinam and Guyana and in the formation of mylonite zones along the BGB.

3.1.2 Granulite domains

In the Guiana Shield four large granulite-facies domains have been recognized: the Imataca belt in the northwest (Venezuela), the Amapá Block at the eastern boundary (Brazil), and the Cauarane-Coeroeni belt and Bakhuis Granulite Belt near the centre (Fig. 3.3). The Archaean Imataca complex is an east-north-east trending horst, which consists predominantly of felsic and mafic granulites, migmatised orthoand paragneisses, and minor amounts of iron formations (Dougan, 1974; Tassinari et al., 2004). A differentiated calc-alkaline magmatic series has been identified as main protolith for the Imataca Complex (Dougan, 1974; Tassinari et al., 2004). Age determinations have indicated a complex Archaean-Paleoproterozoic history, with granulite-facies metamorphism at 2.05-1.98 Ga and amphibolite-facies metamorphism at 2.01-1.96 Ga (Tassinari et al., 2004). Another large Archaean domain, with granulitic ortho- and paragneisses, occurs in the Amapá Block in southern Amapá (e.g., Avelar, 2002; da Rosa-Costa et al., 2006, 2008). The domain might be larger than indicated on Figure 3.2, as its geographical boundaries to the north-west are poorly constrained. Da Rosa-Costa et al. (2008) obtained an age of 2.10-2.09 Ga for the granulite-facies metamorphism. However, smaller Archaean areas near the Amapá block have a different history, with slightly younger ages for granulite-facies metamorphism and charnockitic magmatism (Avelar et al., 2002; Oliveira et al., 2002; da Rosa-Costa et al., 2006).

The Cauarane-Coeroeni Belt (CC in Fig. 3.2) is a sinuous megastructure which stretches over 1,000 km from Coeroeni in south-western Surinam across southern Guyana (Kanuku complex) to Cauarane in the Brazilian state of Roraima (Fraga et al., 2008). The Coeroeni Gneiss in Surinam is composed of amphibolite- and granulite-facies metamorphic rocks of predominantly metasedimentary origin, mainly quartzofeldspathic gneisses and pelitic gneisses with minor amphibolites (Kroonenberg, 1976). Synkinematic metamorphism occurred at 2.01–1.99 Ga (de Roever et al., 2010). The Kanuku complex in southern Guyana is a dome-shaped horst (Berrangé, 1977; Gibbs & Barron, 1993). It is composed largely of paragneisses that have experienced amphibolite-facies metamorphism in the east and south-east, and granulite-facies metamorphism in the west (Berrangé, 1977). The gneisses show compositional banding, isoclinal folding and widespread migmatisation. Granulite bodies in the west part of the complex are fairly homogeneous and may have been derived from magmatic rocks, probably tonalitic bodies intruded into the gneisses under granulite-facies conditions (Gibbs & Barron, 1993). The Cauarane area in Brazil, the western part of the belt, is also mainly composed of high-grade metamorphic supracrustal rocks (Fraga et al., 2008, 2009). High-grade metamorphism and deformation were dated at about 2.00-1.99 Ga (Fraga et al., 2009).

The BGB is a NE-trending belt of banded granulites and metapelitic rocks with metadolerite dykes and locally charnockites (de Roever, 1973, 1975; de Roever et al., 2003). Geochronological data indicate an age of 2.07-2.05 Ga for granulite-facies metamorphism (de Roever et al., 2003). Initially, the Cauarane-Coeroeni belt and BGB were thought to belong to a single "Central Guyana Granulite belt" (Kroonenberg, 1975). However, high-grade metamorphism in the BGB is older than in the Coeroeni and Cauarane areas (Delor et al., 2003; de Roever et al., 2010), implying that the BGB should not be assigned to the "Central Guyana Granulite belt". A more detailed description of the BGB is given below (section 3.3).

3.2 Regional Geology of Western Surinam

IJzerman (1931) was the first geologist to study the geology and petrology of Surinam in detail. During the 1950s to 1970s, geologists of the Geological and Mining Service of Surinam (G.M.D.) mapped the country. The geological map of Surinam at scale 1:500,000 was completed in 1978. The western part of Surinam is largely occupied by biotite granite, subvolcanic granite and acid metavolcanics. The latter rocks are part of an acid volcano-plutonic suite formed during a late phase of the Transamazonian orogeny (1.99-1.97 Ga; de Roever et al., 2010). The biotite granites postdate the other rocks, as suggested by the presence of xenoliths of acid metavolcanics (Bosma et al., 1978, 1984). Northwest of the Bakhuis Granulite Belt and locally to the SE, greenstone sequences occur, and at both sides of the BGB areas with predominantly biotite gneiss are present. The Transamazonian basement is cut by large dolerite and gabbro sills and dykes of the so-called Avanavero type, dated around 1.8 Ga (Norcross et al., 2000; Santos et al., 2003), and by smaller dykes of the Apatoe type, formed at around 200 Ma (Priem et al., 1986; Deckart et al., 2005). In northern Surinam the Precambrian basement described above is unconformably overlain by a Mesozoic-Cenozoic unmetamorphosed sedimentary cover.

3.3 Bakhuis Granulite Belt

The Bakhuis Granulite Belt has a SW-NE direction, oblique to the dominant direction of the greenstone belt, which is more or less parallel to the coast (Fig. 3.2). The belt is 30-40 km wide and 100 km long and consists dominantly of banded granulites. The SW part of the BGB is dominated by charnockites with some mafic intrusives and shows subordinate granulites and pelitic gneisses. The BGB is characterised by an exceptionally high grade of metamorphism, locally with temperatures exceeding 1,000°C (de Groot, 2008).

3.3.1 Horst-like and dome structure

The BGB has a dome-like structure (de Roever, 1973; Dahlberg, 1973; de Roever et al., 2003), in particular indicated by the orientation of pelitic lenses and banding in the northeast of the belt and to a lesser extent by the orientation of banding in the SW (Fig. 3.4). At the south-eastern side of the BGB this dome shape is clearly cut by a steep mylonitic shear-zone, especially visible -on the map- at the Fallawatra occurrence in the NE. A similar zone bounds the BGB at its north-western side. The shear zones have been formed during the Nickerie Tectonometamorphic Episode, dated at 1,200±100 Ma (Priem et al., 1971, 1982). At present, the belt is incorporated in a horst-like structure with a northeast-southwest orientation and with elevations up to 500 m. The faults bounding the horst coincide with the older mylonite zones. Indications have been found for several vertical movements during the Tertiary.

3.3.2 Lithology of the Bakhuis Granulite Belt

Banded granulites are the dominant lithology in the Bakhuis Granulite Belt (de Roever, 1973, 1975; Bosma et al., 1978, 1983). The granulites show a pronounced and omnipresent compositional banding at centimetre to metre scale (Fig. 3.5a), enhanced by incipient migmatisation and by preferred orientation of mafic minerals. Main types are intermediate and mafic granulites, generally with a granoblastic structure. Pelitic gneisses form mappable intercalations among the granulites. Intermediate granulites consist essentially of opx + (antiperthitic) $pl + qz \pm cpx \pm hbl \pm bt \pm kfs$, with accessory magnetite, Fe-Ti oxide and apatite. Felsic types consist dominantly of pl + qz with subordinate opx, and darker types contain additional cpx and hbl. Felsic granulites with dominant kfs or mesoperthite are relatively rare. Mafic granulites contain variable amounts of hbl + bt besides opx and cpx, comprising pyroxene ampibolites as well as nearly hbl-free granulites with abundant pyroxene. Coarse metamorphic minerals in the pelitic gneisses are sil, Mg-rich crd, opx, bt, grt, qz, plagioclase or antiperthite or mesoperthite, and perthite, with accessory opaque minerals, green spinel and in rare cases corundum.



Figure 3.4 Geological map of the Bakhuis Granulite Belt in NW Suriname. Numbers indicate the ages of analysed geochronological samples by de Roever et al. (2003). The Fallawatra area in the north-eastern part of the belt is shown by a circle and two possible UHT remnants in the south-western part by asterisks. Thin black lines indicate the strike of foliation. *Figure from De Roever et al. (2003)*.

The compositional banding of the granulites is indicative of a supracrustal origin whilst intercalations of pelitic gneiss, quartzite, calc-silicate rock and graphite-bearing bands, reflect a metasedimentary nature (de Roever, 1973, 1975). Abundant and wide-spread orthopyroxene was formed by granulite-facies metamorphism. The metamorphism not only produced orthopyroxene in mafic granulites, but also in intermediate and felsic granulites and even pelitic gneisses.

Isoclinal or tight folding of the banding, with steeply plunging fold axes, is common and represents intense syn-metamorphic deformation. At a regional scale, the banding is mostly steeply dipping. Small-scale, incipient migmatisation of the granulites occurs in the form of thin granoblastic, orthopyroxene-bearing quartz-plagioclase leucosomes parallel to the banding (Fig. 3.5b) and in the form of cross-cutting veins of similar composition. This indicates that migmatisation took place under relatively anhydrous granulite-facies conditions. Narrow metadolerite dykes are present throughout the BGB (Fig. 3.5c; de Roever, 1973; de Roever et al., 2003). Two types occur: foliated pyroxene amphibolite dykes that display some deformation indicative of a synkinematic character, and presumably postkinematic straight and discordant dykes with relict igneous textures.

The south-western part of the belt consists mainly of charnockite (orthopyroxene granite), together with numerous gabbroic-ultramafic bodies, and smaller occurrences of banded granulite and pelitic gneiss in between. The charnockites show an undisputedly igneous character with a typical mineral assemblage of qz + pl + afs + opx + cpx + bt. Green to brown-green hbl is frequently present, and opaque ore



Figure 3.5 Field photographs of characteristic lithological features in the Bakhuis Granulite Belt. Pencil of 13 cm for scale. **a.** Preferential weathering displays compositional banding in granulites. (FN56) **b.** Leucosome (beige part) and melanosome (dark grey part). **c.** Metadoleritic dyke cross-cutting mesoperthite granulite (FN44); **d.** Massive field appearance of charnockites at Moi-Moi, SW BGB.

minerals, zircon and apatite are very common accessory phases. The charnockites can easily be discriminated from the granulites while they form homogeneous, massive outcrops (Fig. 3.5d), whereas the granulites are characterised by ubiquitous compositional banding. Xenoliths are common in the charnockites. In thin-section charnockites can be recognised by large euhedral plagioclase grains that contain zoning and Karlsbad twinning, a feature typical for magmatic grains. The charnockites have been investigated at the VU University Amsterdam (Klaver, 2011). Small gabbroic and ultramafic bodies are also abundant in the south-western part of the BGB.

3.3.3 UHT metamorphism in the Bakhuis Granulite Belt

3.3.3.1 Mineral assemblages and metamorphic conditions

The special feature of the Bakhuis Granulite Belt is the exceptionally high grade of metamorphism. In the 1970s, de Roever (1975a,b) presented the first evidence, based on samples taken by the Geological and Mining Service of Surinam in the 1950s and 1960s. Mineral assemblages such as opx-sil-qz and sapphirine-quartz were found, which are now known to be characteristic for UHT metamorphism (Harley, 1998a). A detailed description of typical UHT assemblages from the belt, their chemical composition and age (de Roever et al., 2003) was not picked up by review papers on the occurrence of UHT metamorphism throughout the world (Kelsey, 2008; Brown, 2007). The main occurrence of opx + sil and spr was found in the NE part of the BGB, in a metapelite area of 50-100 km² (circle marked UHT on Fig. 3.4). De Roever et al. (2003) reported sapphirine in contact with quartz and sapphirine in quartz-rich rocks. UHT conditions were also indicated by the common presence of the assemblage opx + sil + qz and 8-10wt% Al₂O₃ in the opx, which exceeds the 8wt% lower limit required for UHT opx.

In the BGB the characteristic UHT mineral assemblages occur in metapelitic rocks. Evidence for UHT metamorphism was not found in the granulites, in which the pelitic gneisses are intercalated. Moreover, pelitic gneisses outside the Fallawatra occurence do not show the common presence of opx + sil or spr. This may be the result of the extensive retrograde metamorphism shown by most metapelitic rocks in the BGB. Remnants of UHT assemblages were found at two locations in the SW part of the BGB (asterisks in Fig. 3.4; de Roever et al., 2003). One sample shows coarse spr-crd symplectite adjacent to coarse sillimanite, probably formed at the expense of orthopyroxene. A sample from the other location in the SW contains opx accompanied by sil. Furthermore, corundum was found in qz-rich, metapelitic rocks, even in direct contact with quartz.

Based on the petrological data available, an attempt has been made to construct a P-T path for the north-eastern UHT occurrence (Fig. 3.6; de Roever et al., 2003). The P-T path is counter clockwise with a near-isobaric cooling path. One of the arguments for such a path was the peculiar occurrence of sapphirine. Small amounts of sapphirine were found in many orthopyroxene-sillimanite gneisses, but sapphirine was never found in contact with orthopyroxene, suggesting that it belonged to an earlier assemblage. An early assemblage of crd + sil (I) is assumed to have been replaced by the peak-T assemblage spr + qz (II). Initial cooling is represented by the assemblage opx + sil + qz (III).

Geothermo(baro)metry to determine metamorphic conditions for the Fallawatra occurrence was carried out in an MSc project at VU University Amsterdam (de Groot, 2008). The results confirmed that metamorphism occurred there under UHT conditions and established peak temperatures as high as 1000-1050°C. It was not possible to obtain a reliable estimate of the pressure at which UHT metamorphism occurred.

3.3.3.2 Age of metamorphism

In the BGB Pb-Pb zircon evaporation data provide an age range of 2,055-2,072 Ma for the high-grade metamorphism, including UHT metamorphism (de Roever et al., 2003). Pb-Pb dating was performed on a grt-sil gneiss, two grt-bearing gneisses an intermediate granulite. and Furthermore, two synkinematic metadolerites and a charnockite were dated. In addition, zircon from two samples, a grt-sil gneiss and a granulite, were subjected to U-Pb SHRIMP analysis, which gave similar ages (Lafon, pers. comm.). The dated samples all came from the east-central (Blanche Marie Falls) and north-eastern parts of the BGB. The age of high-grade metamorphism in the BGB is significantly younger than the 2.18-2.13 Ga metamorphism in the TTG-greenstone belt (Delor et al., 2003).



Figure 3.6 Pressure-Temperature diagram displaying a counter clock-wise P-T path constructed for the UHT occurrence in the north-eastern part of the Bakhuis Mountains, with assemblages $I \rightarrow II \rightarrow III$ (from de Roever et al., 2003). The P-T diagram is for high fO_2 metapelites in the KFMASH system grid. Abbreviations: bt – biotite, crd – cordierite, grt – garnet, ky – kyanite, opx – orthopyroxene, qz – quartz, spl – spinel, sil – sillimanite, spr – sapphirine.

The geochronology of the BGB was found to be more complicated as charnockites in the SW part of the belt yielded zircon U-Pb LA-ICP-MS ages of about 1,980 Ma, postdating UHT metamorphism by about 70 Myr (Klaver, 2011). The charnockites are thought to have derived from partial melting of granulites. The high crystallisation temperature of the charnockites, 950-1000°C, suggests that a second ultrahigh-temperature event affected the BGB. It should be noted that this episode is not necessarily a metamorphic event.

3.3.3.3 Heat source for metamorphism

As mentioned in section 2.3, several tectonic settings have been invoked to explain the occurrence of UHT metamorphism. A model involving a back-arc setting is not relevant for the BGB as it is not situated in the back arc of the Greenstone Belt. Delor et al. (2003) place the UHT metamorphism in the BGB in a time and tectonic context and argue that UHT metamorphism occurred as a response to a late-Transamazonian, mantle-driven thermal perturbation (upwelling asthenosphere) in a zone of maximum crustal stretching. The presence of synkinematic metadolerite dikes in the banded granulites constitutes sound evidence that mafic magmas were present at the time of UHT metamorphism. This hot, anhydrous basaltic magma might indeed have provided a heat source for UHT metamorphism, but it is doubtful whether the rather small amount of magma found would have provided sufficient heat. Furthermore, a counterclockwise path of UHT metamorphism as deduced for the area in the NE of the BGB (de Roever et al., 2003) is often interpreted as being the result of magmatic underplating (e.g., Wells, 1980).

4. GEOTHERMO(BARO)METRY

4.1 Introduction

For the study of metamorphism it is a prerequisite to obtain a reliable determination of temperature and pressure conditions. Modelling, the state-ofthe-art method, was originally part of this study but could not be carried out due to time constraints. Therefore, this study used conventional geothermo(baro)metry, which will be reviewed in this chapter.

Geothermobarometry relies upon the fact that equilibrium mineral pairs/ assemblages may vary their chemical composition as a function of temperature and pressure. The distribution of exchanged components (K or K_D) can be expressed as a function of T and P:

$$\ln K = \Delta G^0 / RT$$



Figure 4.1 Schematic P-T diagram illustrating general characteristics of geothermo- and barometers. Geothermometers have steep slopes and geobarometers have shallow slopes on a P-T diagram.

where ΔG^0 is the Gibbs free energy of the reaction

for the pure phases at the pressure and temperature of interest, and *R* is the thermodynamic gas constant. Geothermobarometers represent this relation as lines of K in P-T space, using the analysed mineral chemistry of the equilibrium assemblage (Fig. 4.1). Conventional geothermo(baro)meters can be used to determine the temperature and/or pressure of metamorphic rock formation. This may, however, not hold if extreme conditions are involved. Many geothermo(baro)meters have been found to be unsuitable for P-T analysis of UHT metamorphism, due to the very high temperature implied, in many cases above 1000°C, and because the rocks often cooled down relatively slowly from these very high temperatures. During cooling retrograde mineral re-equilibration takes place and as a result considerably lower closure temperatures of intercrystalline diffusion are found rather than the equilibrium temperature at which the mineral assemblage actually developed (Harley, 1984, 1989; Frost & Chacko, 1989; Fitzsimons & Harley, 1994; Pattison & Begin, 1994).

In particular geothermometers based on Fe-Mg exchange show this problem, because of continuing Fe-Mg exchange below their closure temperature. Fe-Mg ion exchange between minerals is faster than Al and/or Si exchange and so may continue after the cessation of effective Al and/or Si exchange or nettransfer (e.g., Harley, 1989; Frost & Chacko, 1989; Fitzsimons & Harley, 1994; Pattison & Begin, 1994; Pattison et al., 2003). Also the well-known two-pyroxene solvus thermometer which is based on Ca-Mg-Fe exchange (e.g., Lindsley, 1983; Fonarev et al., 1991) presents large difficulties in UHT metamorphism due to re-equilibration during cooling and usually indicates relatively low closure temperatures. This is the main reason why two-pyroxene thermometry has not been used in this study to estimate the P-T conditions of the mafic and intermediate granulites which constitute the bulk of the BGB. Thermometers that are partly based on Mg/Fe exchange will often also be unreliable. An example is the Opx-Grt Al barometer (Harley & Green, 1982; Aranovich & Berman, 1997). Pressure estimates will increase as the temperature calculated using the Grt-Opx Fe-Mg exchange thermometer decreases. As a result of this feedback effect, not peak pressures but closure pressures are estimated (Fitzsimons & Harley, 1994). However, peak temperatures might still be derived through the use of retrieval calculations that involve back calculation of the Fe-Mg compositions (Fitzsimons & Harley, 1994; Pattison & Begin, 1994; Pattison et al., 2003).

Ternary feldspars are a common constituent of granulite-facies rocks and are fairly resistant to retrograde resetting, except for Na-K exchange. The thermometry of ternary feldspars is extremely useful

to studies of UHT metamorphism, as feldspars are not subject to oxidation, a problem of mafic geothermometers. Therefore, feldspars can provide evidence for UHT metamorphism in terranes that have a poor or ambiguous record of UHT conditions on account of mafic minerals. In addition, the solubility of alumina in orthopyroxene is an important geothermometer in UHT metamorphic terranes. These geothermometers will be discussed below.

4.2 Ternary Feldspar Thermometry

4.2.1 Ternary feldspar system

The feldspar system can be considered as a ternary system composed of anorthite, CaAl₂Si₂O₈, albite, NaAlSi₃O₈, and orthoclase, KAlSi₃O₈. At elevated temperatures the feldspar system forms a ternary solid solution over a substantial part of the Ab-Or-An system. Two end-member binaries show complete miscibility, plagioclase (Ab-An) and alkali feldspar (Ab-Or). In plagioclase the solubility of Or is very limited and strongly dependent on temperature, as is the solubility of An in alkali feldspar. Consequently, a large miscibility gap in the Or-An binary is created that extends deep into the ternary field. Exsolution of plagioclase lamellae from an alkali feldspar host is known as perthite. A ternary grain consisting of an equal amount of exsolved plagioclase and alkali feldspar is called mesoperthite, whilst antiperthite refers to a plagioclase host with exsolved alkali feldspar lamellae. The extent of solid solution of anorthite in alkali feldspar and of orthoclase in plagioclase is strongly controlled by the temperature of crystallisation (e.g., Barth, 1951). Feldspar geothermometry is based on this temperature dependency. The geothermometer can be applied to a pair of plagioclase and alkali feldspar as well as to single hypersolvus feldspars. A feldspar pair defines two intersections with the solvus at a specific temperature, whilst a single feldspar will define a point on the solvus or at a higher temperature (hypersolvus). Hypersolvus feldspars will therefore provide minimum temperatures only. However, these temperatures are thought to closely approach peak conditions (Hokada, 2001; Martignole & Wang, 2010).

The strong temperature dependency was first recognised and empirically calibrated by Barth (1951) and has been thoroughly studied in the succeeding decades (e.g., Seck, 1971a,b; Fuhrman & Lindsley, 1988; Elkins & Grove, 1990; Benisek et al., 2010), resulting in more sophisticated thermodynamic models. Hokada (2001) was the first to recognise the significance of ternary feldspar thermometry for the study of UHT metamorphism. Hokada's study and many other studies of UHT metamorphism showed feldspar temperatures that could be confirmed with the aid of other geothermometers and/or modelling (e.g., Hokada, 2001; Rötzler & Romer, 2001; Štípská & Powell, 2005; Jiao & Guo, 2011). In many cases peak temperatures in excess of 1000°C were found in these studies. Nowadays, feldspar thermometry is a widely recognised method in studies of UHT terranes and other high-temperature rocks.

It is important to establish the origin of the ternary feldspar should be established, because exsolved ternary feldspar in metamorphic rocks might have been inherited from an igneous precursor. Thermometry would then indicate the precursor temperature rather than the metamorphic temperature. In this study, ternary feldspars in the metapelitic rocks are undoubtedly of metamorphic origin because the protolith is sedimentary. This is less clear for ternary feldspar in the mesoperthite granulites. However, no evidence of magmatic precursors has been found in these highly leucocratic rocks.

4.2.2 Ternary feldspar solvus models

A program explicitly developed for feldspar thermometry is SOLVCALC (Wen & Nekvasil, 1994). The program is a user-friendly interactive graphics software for calculating the ternary feldspar solvus and for two-feldspar thermometry. This study used the program to calculate ternary feldspar solvus curves with an interval of 10°C which were exported into a ternary feldspar Ab-Or-An plot (Fig. 4.2). Pressure has to be defined in the program, but has only a small influence of $<5^{\circ}$ C/kbar on temperature (e.g., Fuhrman &

Lindsley, 1988). The program can calculate ternary feldspar isotherms for different models, Ghiorso (1984), Green & Usdansky (1986), Nekvasil & Burham (1987), Fuhrman & Lindsley (1988), Lindsley & Nekvasil (1988), and Elkins & Grove (1990). The models describe the thermodynamic mixing behaviour of ternary involving expressions feldspar. for configurational entropy (ideal part of activity terms) and for excess free energy (activity coefficients). Each of these models has advantages and weaknesses and it should be carefully considered which one is most appropriate for a specific study. Different models may result in significant temperature differences.

In this study the model developed by Fuhrman & Lindsley (1988; hereafter named as



Figure 4.2 An–Ab–Or ternary feldspar diagram with solvus curves at 800-1200°C calculated at 8.5 kbar using the model of Fuhrman & Lindsley (1988).

FL model) is preferred. The FL model takes the Al-Si ordering of the so-called Al-avoidance into account (e.g., Newton et al., 1980; Myers et al., 1998). It considers the equilibrium of all three components (An, Ab and Or) in coexisting alkali and plagioclase feldspars, which is better than treating the feldspar solution as an ideal single-site mixing. The FL model is primarily based on the experiments of Seck (1971a,b), which were performed at 1, 5 and 10 kbar, whereas Elkins & Grove (1990) only performed experiments at 1-3 kbar and calibrated these with the experiments of Seck (1971a,b). Additionally, Fuhrman & Lindsley (1988) refined the experiments of Seck (1971a,b) and added high temperature experiments up to 850°C. This makes their model appropriate for high-temperature conditions. Štípská & Powell (2005) argue that the experimental data used in the then existing models (Fuhrman & Lindsley, 1988; Elkins & Grove, 1990; Benisek et al., 2004; Holland & Powell, 2003) do not represent the full range of temperature and pressure of formation of natural ternary feldspars. They argue that the FL model ignores the structural LT/HT transition in plagioclase, which makes extrapolation of their model problematic. Holland & Powell (2003) model the structural transition, but fail to incorporate other important parameters. Štípská & Powell (2005) conclude that a satisfactory model is yet to be constructed and that for temperatures around 1000°C at 8 kbar the FL model looks most appropriate. Recently, Benisek et al. (2010) constructed a model based exclusively on calorimetric and volumetric measurements, distinctly different from the models mentioned (hereafter named B model). They argue that their model is better than a phase-equilibrium based mixing model, such as the FL model. Until present the B model has not been extensively used for UHT studies. The only example in which the FL and B model are compared is a study by Jiao & Guo (2011). With the B model Jiao & Guo (2011) obtained unreasonably low temperatures of 400-500°C for their ternary feldspars, compared to 900-1000°C using the FL model. Furthermore, they demonstrate that based on the B model perthite yields a higher temperature than mesoperthite, which they consider to be unlikely. Jiao & Guo (2011), therefore, conclude that the model of Benisek et al. (2010) is unsuitable for their data. For the time being, the best model for this study appears to be the FL model.

Another reason to use the FL model is that it has been used for feldspar thermometry in most studies of UHT metamorphism (e.g., Hokada, 2001; Štípská & Powell, 2005; Hokada & Suzuki, 2006; Prakash et al., 2006; Pilugin et al., 2009; Martignole & Wang, 2010; Jiao & Guo, 2011). The feldspar thermometry data of these studies were in overall agreement with results of other thermometric methods such as Al-in-opx and/or pseudosections. Use of the FL model facilitates comparison of the BGB feldspar thermometry data with the results of other UHT terranes.

4. GEOTHERMO(BARO)METRY

4.3 Al-in-orthopyroxene Thermometry

A high Al_2O_3 content in orthopyroxene (8-13wt%) coexisting with garnet or another aluminium-rich phase, such as sil, spr and crd, is one of the most reliable indicators of high metamorphic temperatures (Harley, 1989, 1998a, 2008). This is mainly because Al solubility is relatively resistant to post-peak reequilibration. Harley & Green (1982) were the first to experimentally calibrate a geothermobarometer for granulites based on the temperature dependency of Al solubility in orthopyroxene in coexistence with garnet. Another commonly used opx-(grt) thermometer has been developed by Aranovich & Berman (1997). The latter thermometer, although more refined in a thermodynamic sense, is influenced by the feedback effects of Fe-Mg exchange upon cooling and as a consequence generally yields lower temperatures (30-50°C; Harley, 2008). Aranovich & Berman (1996) also constructed a P-T diagram in FMAS containing isopleths of Al₂O₃ content of orthopyroxene. On the base of the Al-content in orthopyroxene and an adopted pressure, one can graphically obtain a temperature estimate. Other phase diagrams are contoured for the Al level in opx, as well. Most of these diagrams show the composition of garnet and orthopyroxene in relation to P and T, for the assemblage grt + opx + sil + qz at higher pressures and the assemblage grt + opx + crd + qz at lower pressures (e.g., Harley, 1989; Hensen & Harley, 1990, 1998; Harley & Motoyoshi, 2000), whereas some other studies focused on the coexistence of opx with other Al-rich phases, such as sapphirine (e.g., Arima & Onuma, 1977; Hollis & Harley, 2003).

Although the aluminium solubility in orthopyroxene is considered to be a reliable thermometer, estimated peak temperatures can vary considerably depending on the data sets and experiments used. Temperature differences can reach up to 70°C (Podlesskii, 2006). In addition, the commonly used Alisopleth diagrams are only valid for orthopyroxene formed in a reduced system with insignificant ferric iron (e.g., Harley, 2008). The incorporation of Fe³⁺ instead of Al expands the stability of mineral assemblages with e.g., opx, to significantly lower temperatures relative to the purely Al-based stability fields (e.g., Kelsey et al., 2006; Diener & Powell, 2010). If the Al-in-opx phase diagrams are to be used for oxidised rocks, the presence of Fe³⁺ will decrease the amount of alumina attributed to the Tschermak-component (MgAlAlSiO₄) and increase the X_{Mg} of orthopyroxene or Al/2 per *n* cations will not be suitable for oxidised systems. Instead of the Al₂O₃ level of orthopyroxene or Al/2 per *n* cations will not be suitable for oxidised systems. Instead of the Al₂O₃ level, the amount of Tschermak component, i.e., the level of Al in the Y position, should be taken into account in the diagrams. As mentioned above, the influence of ferric iron may be larger due to expansion of the opx stability field to lower temperature. However, according to Harley (2008), the effect of small amounts of ferric iron in orthopyroxene, Fe³⁺/Fe^{tot} < 0.12, would reduce the Al-in-opx temperature by only 20-50°C.

The BGB witnessed oxidising conditions during granulite-facies metamorphism (de Roever et al., 2003). Consequently, application of the Al-in-opx thermometer would produce less meaningful results. However, it is not the purpose of this study to use Al-in-opx thermometry to estimate P-T conditions for the BGB. The temperature will be determined with the aid of ternary feldspar thermometry. Based on the criterium given by Harley (1998a, 2008) that orthopyroxenes with 8wt% Al₂O₃ or more are diagnostic of UHT metamorphism, this study will established whether orthopyroxenes present in the BGB are characteristic for UHT metamorphism or not. It should be kept in mind that this holds only for mineral assemblages that witnessed low oxidising conditions.

An ideal method to employ the solubility of alumina in opx as thermometer would be to use thermodynamic modelling to construct pseudosections contoured for Al content in opx (e.g., Kelsey et al., 2004; Brandt et al., 2011). This approach is similar to the Al isopleths in phase diagrams (e.g., Hensen & Harley, 1990; Harley, 1998a), but much more specific as it is calculated for a specific rock composition. This method would be even more useful for oxidised rocks such as in the BGB, if thermodynamic calculations take ferric iron into account.

4.4 Other Geothermometry

4.4.1 Ti-in-quartz thermo(baro)metry

The temperature dependence of titanium incorporation into quartz, in coexistence with rutile or other Ti phases, provides a potentially powerful single-mineral thermometer, TitaniQ (Wark & Watson, 2004, 2006; Thomas et al., 2010). Quartz is a very common mineral and consequently the thermometer has a wide application to igneous and metamorphic rocks. Most studies have found reasonable consistency between the Ti-in-quartz thermometer and traditional thermobarometers for metamorphic rocks at temperatures above 500°C (Wark & Watson, 2004, 2006; Spear & Wark, 2009; Storm & Spear, 2009). However, some studies noted inconsistencies (e.g., Raimondo et al., 2011; Kidder et al., 2013). Moreover, the geothermometer does not seem to be applicable to all metamorphic rocks and the method itself is still debated (Thomas & Watson, 2012; Wilson et al., 2012).

An attempt had been made to apply the Ti-in-quartz thermometer to BGB rocks at the VU University Amsterdam (de Groot, 2008). Two methods were investigated. One method was based on ICP-analysis of Ti-bearing quartz grains from pelitic gneisses of the UHT area in the NE part of the BGB. ICP-analysis showed a quite low Ti level in the quartz, corresponding to a temperature of approximately 750°C. A fraction with relatively clear quartz grains used, whilst the fraction with more inclusions might have provided better results. The other method examined is electron microprobe analysis of the Ti level in quartz. This method has provided good results for Ti-bearing quartz without exsolution in UHT rocks (Wark & Watson, 2006; Altenberger et al., 2012). However, quartz in BGB granulites and gneisses shows wide-spread exsolution of minute rutile needles. EMP analysis with a defocussed beam most probably would not be able to cover sufficiently large quartz areas with Ti exsolution (Lustenhouwer, *pers. comm.*). In view of these problems, the Ti-in-Q method has not been applied in this study.

4.4.2 Ti-in-zircon thermo(baro)metry

The temperature dependence of Ti substitution for Si in zircon in the presence of rutile or other Ti phases provides a powerful single-mineral geothermometer (e.g., Watson et al., 2006). Zircon is a common accessory mineral and consequently a thermometer based on the Ti content of zircon should have wide application to igneous and metamorphic rocks. However, the Ti-in-zircon thermometer may not record high- to ultrahigh-temperature metamorphism, because zircon crystallisation does not always coincide with the thermal maximum (e.g., Baldwin et al., 2007; Fu et al., 2008; Harley, 2008).

The Ti-in-zircon thermometer was applied to charnockites in the BGB, for which crystallisation temperatures of 950-990°C had been determined (Klaver, 2011). The titanium levels in zircons were quite low and variable, resulting in considerably lower temperatures. In addition, the analysed zircon is associated with Ti-bearing opaque minerals, most likely ilmenite and magnetite, instead of rutile. The pelitic gneisses and granulites in the BGB also contain abundant opaque minerals rather than rutile. Therefore, the Ti-in-zircon thermometer is not expected to provide valuable results and has not been used for this study.

4.5 Geobarometry

Commonly used geobarometers for metapelitic rocks (e.g., grt-opx - Harley & Green, 1982; grt-qz-pl (GASP) – Newton & Perkins, 1982) require the presence of garnet. In BGB metapelitic rocks garnet is in most cases markedly younger than the granulite-facies metamorphism and/or has formed at the expense of peak metamorphic minerals such as spr. However, the composition of orthopyroxene in coexistence with an Al-rich phase might be used for geothermobarometry. Where $X_{Al(Opx)}$ contours are nearly vertical in P-T space and, therefore, suitable as geothermometer, the Mg content is an excellent pressure indicator

as the X_{Mg} isopleths are sub-horizontal in P-T space. Hensen & Harley (1990) did not only determine $X_{Al(Opx)}$ isopleths for granulite-facies conditions, but combined these with $X_{Mg(Opx)}$ isopleths. Although their petrogenetic grid is based on the assemblage opx + grt, it can also be used if orthopyroxene is associated with another Al-rich phase, such as sillimanite (Tamashiro et al., 2004; Tateishi et al., 2004). In this study the pressure will be determined with the diagram of Tateishi et al. (2004) which is based on isobars and isotherms from Hensen & Harley (1990). It should be kept in mind that the assemblages studied are oxidised, whereas the method of Hensen & Harley (1990) was developed for a reduced system.

5. METHODS

5.1 Sampling Strategy and Selection

During three weeks of fieldwork in February 2012, samples of pelitic gneisses were collected from several areas within the BGB. The main aim of fieldwork was to collect samples throughout the whole Bakhuis Granulite Belt (BGB) in order to find a) exsolved ternary feldspar for thermometry, and b) UHT metamorphic minerals such as orthopyroxene and sapphirine, and other minerals of interest, like cordierite, corundum and spinel.

Sampling in the belt is challenging for several reasons and a specific approach is required. The Bakhuis Mountains are covered by tropical rain forest (Fig. 5.1a), resulting in deep weathering, poor exposure and limited accessibility (Fig. 5.1b). Therefore, systematic fieldwork and sampling was not possible. Furthermore, only a small part of the belt could be reached. Good outcrops are located along rivers (Fig. 5.1c) and in smaller streams on hill slopes, where water has been able to deeply incise and consequently expose the rocks. Small trails were cut through the jungle on the river banks, if river outcrops were under water. At two locations a trail of several km was cut inland to reach metapelite zones. Despite the poor exposure and limited accessibility many suitable outcrops could be found, using the geological map of Surinam and the detailed maps with sample locations from the 1960s and 1970s. Fresh, representative samples were taken, with a weight of $<\frac{1}{2}$ kg if the goal was to make thin-sections and a weight of > 1 kg for XRF. For many locations more than one sample was taken as most minerals of interest, crd, spr and mesoperthite, cannot be recognised in the field. If separate leucosome layers were present, the leucosome was sampled, as well, for feldspar analysis. The samples were given numbers starting with FN, after Fienke Nanne, and for each sample location GPS coordinates were taken (Appendix A.I). Samples collected from the same location received an additional A, B, etc. In total 104 samples, FN01-FN87D, were collected at 47 different locations in the field, with a combined weight of \sim 80 kg. Besides metapelites also felsic granulites and some other interesting rock-types, such as sillimanite-cordierite granodiorite, were sampled. The sillimanite-cordierite granodiorite (FN60) and a mesoperthite granulite (FN69) were sampled in a quantity of 3-5 kg in order to perform U-Pb zircon dating and XRF analysis. A similar quantity of a sillimanite gneiss (MKS 40) had been taken in October 2011 for U-Pb zircon dating. The location, in the Kabalebo River, was just under water in February 2012, preventing further sampling.

As mentioned above, the main objective of the field campaign was to collect metapelitic rock samples suitable for ternary feldspar analysis throughout the entire BGB. However, it was only possible



Figure 5.1 Characteristic fieldwork situations in the Bakhuis Granulite Belt. **a.** Coverage of dense tropical rain forest. **b.** Infrastructure. **c.** Most common type of outcrop, along a river.

to collect samples in the northeast, (northern) centre and south-western, around Kabalebo, part of the belt (see Fig. 6.1). The remainder of the belt is not directly accessible, requiring an expensive expedition to reach a location. For the inaccessible parts of the BGB this study used samples that were collected in the past. The belt was extensively sampled in the 1960s and 1970s by the Geological and Mining Service of Surinam (GMD). All samples taken were studied by E. de Roever at the GMD for the geological map of the belt. During two expeditions prof. Dr. H.N.A. Priem collected samples for geochronology. Furthermore, diamond drilling was carried out by the GMD at several locations in the belt for base metal exploration. The GMD provided small parts of drill cores for this study. From the Natural History Museum Naturalis at Leiden samples from the expeditions of prof. Dr. H.N.A. Priem and some samples from expeditions around 1900 were borrowed. E. de Roever provided samples from his private collection of 1972-1977 and of 1997-2000. Additionally, samples gathered for previous VU University Master Theses were used (de Groot, 2008; Klaver, 2011). All samples combined a sufficient coverage of metapelitic rocks and mesoperthite granulites through most of the BGB could be ensured.

5.2 Electron Microprobe Analysis

5.2.1 Introduction

A large part of this study consisted of the compositional analysis of minerals with a Jeol JXA-8800M electron microprobe analyser (EMPA) at the VU University Amsterdam. An electron microprobe performs in situ, (nearly) non-destructive analysis under high vacuum conditions (2⁻⁶ torr; e.g., Reed, 2005). It allows qualitative and quantitative determination of the chemical composition on very small sample areas, down to 1 micron in diameter. Qualitative analyses are performed with an energy dispersive spectrometer (EDS), whilst quantitative analyses are accomplished with several wavelength dispersive spectrometers (WDS). Both techniques rely on the unique atomic structure and hence characteristic set of x-rays of an element. Occasionally, this study used EDS to quickly identify which phase was present, but WDS was dominantly utilised. For each analysis sequence internal mineral standards are used for standardisation while external standards are incorporated to assess the quality of analyses. External standard analyses were in agreement with recommended values (Table 5.1). Raw data were reduced using the ZAF correction method (Armstrong, 1988), which corrects for matrix effects associated with atomic number, absorption, and fluorescence. Subsequently, the totals of the data per analysis were inspected, which should not differ significantly from 100wt%. A low total weight percentage might indicate that elements in the mineral were not analysed. Deviations might also be due to a mechanical error, causing incorrect repositioning or focussing of the beam. Except for water-bearing minerals such as cordierite, analyses with a weight total of <98% and >102% were discarded.

2	1							
External Standard		SiO ₂	AI_2O_3	Na₂O	K ₂ O	CaO	BaO	SrO
Orthoclase (336)	Average (wt%)	64.52	18.12	1.21	14.86	0.02	0.18	0.30
<i>n</i> = 10	(%)RSD 2σ	1.70	5.40	17.99	3.81	49.19	11.94	56.58
	Recomm. value (wt%)	64.20	18.30	1.17	14.95	0.00	0.16	0.00
	Deviation	0.51	-1.00	3.82	-0.57	-	13.92	-
Albite (336)	Average (wt%)	68.46	20.20	11.36	0.13	0.09	0.01	0.27
<i>n</i> = 6	(%)RSD 2σ	1.23	8.94	6.53	9.85	36.68	106.63	79.03
	Recomm. value (wt%)	68.60	19.45	11.60	0.14	0.05	0.00	0.00
	Deviation	-0.20	3.84	-2.08	-8.65	83.31	-	-

Table 5.1 Reproducibility of major elements in two in-house external standards as measured with the EMP (3 μ m beam) at the VU University Amsterdam during feldspar analyses performed for this study.

5.2.2 Feldspar analysis

The largest part of EMP analyses was performed on ternary feldspars. Prior to microprobe analysis more than 80 samples were examined by light microscopy. A total of 20 samples was chosen for EMP feldspar analysis. At least four feldspar grains were selected per sample. For each of the two components in one grain, plagioclase and alkali feldspar, at least 4 spots were analysed in order to assure a representative composition. Analyses of mixed plagioclase and K-feldspar due to poor probe repositioning were omitted. Backscatter electron (BSE) images were taken for each analysed grain for image analysis (see section 5.3). The instrument settings and standards used for feldspar analyses are listed in Table 5.2. Besides the main elements (Si, Al, Ca, Na and K), Sr and Ba have also been analysed. These minor elements were included while Essene et al. (2005) demonstrated that incorporation of Ba and/or Sr extends the stability field of alkali feldspar to lower temperatures. If this effect is ignored, modelling can result in an overestimation of the actual feldspar temperature.

The most challenging part of EMP analysis of feldspar is the analysis of the mobile elements, in particular Na. Sodium is a highly volatile and mobile component, which should be analysed with a low beam intensity in order to prevent migration from the beam excitation volume. The beam intensity is controlled by the beam diameter, beam current and acceleration potential. For this study the beam diameter for feldspar analysis was either set to 3 μ m or 10 μ m. A defocused beam with a diameter of 10 μ m would be optimal, but many lamellae had a width < 10 μ m. For such lamellae a beam diameter of 3 μ m was chosen. In combination with a beam diameter of 3 μ m or 10 μ m, a probe current of ~25 nA and an acceleration voltage of 15.0 kV were used. Sodium was measured first, because when analysed as one of the last elements it could already have migrated. Migration of sodium will be accompanied by a relative increase in the concentrations of the other components, such as Si and Al. This study, therefore, paid extra attention to the sodium data. Inspection of the analyses of external standards such as albite showed an overall agreement with their recommended values (Table 5.1). Therefore, it can be concluded that Na loss during analysis was insignificant.

In some grains feldspar lamellae were thinner than 3 μ m. Therefore, another approach than individual spot analysis had to be used. One analytical technique to analyse a representative area of the **Table 5.2** Instrumental parameters and standards for measurements on the JEOL JXA 8800 M Electron Microprobe at VU University Amsterdam.

	All minerals							
Accelerating Voltage	15 kV							
Beam current	25 nA							
Internal calibration standards	ation BaAl ₁₂ O ₉ 238 (Ba); Celestine 504 (Sr), Chromite 207 (Cr), Corundum 202 (Al), Diopside 303 (Si, Ca), Fayalite 324 (Fe), Illmenite 225 (Ti), Jadeite 304 (Na), Olivine 301 (Mg), Orthoclase 336 (K), Tephroite 325 (Mn)							
Peak counting time	25 seconds (Si, Al, Ca, Mg, Na, K) 36 seconds (Fe, Ti, Mn, Cr, Sr, Ba)							
	Fsp	Grt, Opx	Spl	Crd	Sil, Spr	Crn		
Sample spot size (μm)	3 or 10	2	2	2	2	2		
Measured elements	Si, Al, Na, K, Ca, Sr, Ba	Si, Al, Na, Ca, Ti, Fe, Mg, Mn, Cr	Si, Ti, Al, Cr, Fe, Mn, Mg, Ca	Si, Al, Na, Fe, K, Ca, Mn, Mg	Si, Al, Na, K, Ti, Fe, Mg, Mn, Cr	Al, Cr, Fe, Ti, (Si)		
External standards	Di, Or, Jd, Ab	Di, Alm, Prp, Chr, Ilm, En, Tep, Ol	Ilm, Chr, Ol, Fa, Tep	Di, Crn, Ol, Fa, Tep	Di, Crn, Fa, Tep, Ol	Crn		

Mineral abbreviations follow Whitney & Evans (2010)

grain is by rapid and repeated scanning of the electron beam across this area during one WDS analysis. The areal analysis gives an average composition that should represent the ternary feldspar composition. It is a very fast method and image processing is not required. Another option is to perform mapping analysis, on a rectangular area that is subdivided into a grid of points. Each point is individually measured using a defocused beam of 15 μ m in diameter. The average of all individual spots should represent the ternary feldspar composition. The acquisition time of all points together is much longer than for the previous method, but this technique might be more accurate while each spot is measured individually. Drawback of both techniques is that ZAF correction of the raw microprobe data for the area is carried out assuming that the area and each analysis point is homogeneous, consisting of one phase, whereas in reality the area consists of two different phases, alkali feldspar and plagioclase. A study by Raase (1998) showed that area scans usually underestimate Ca, resulting in temperatures that are too low by about 10- 20° C. Because of this drawback the method was used in this study only if required.

5.2.3 Other minerals

In 17 thin-sections minerals such as orthopyroxene and cordierite were analysed using the electron microprobe. The operating conditions used for each mineral are listed in Table 5.2. For minerals like pyroxene and garnet one has to be aware of zonation. Due to retrograde reactions the rim compositions may not show the original peak-metamorphic conditions and the core values should be taken as representative. However, the 'true' core of a grain does not have to be present in the studied section, as the section location might be in the outer regions of the grain instead of through its core. Therefore, it is better to analyse rather many grains and several spots within the grain. EDS mapping may help to find sections with strong zonation and the zones with the highest level of the element of interest, such as Al in orthopyroxene.

A limitation of the microprobe is that it cannot distinguish the different valence states of iron. If all iron is treated as FeO, a low analysis total and lack of charge balance are the result for Fe^{3+} -bearing minerals. The conventional method to determine Fe^{3+} is by charge balancing the analysis assuming ideal stoichiometry. In this study ferric iron contents for all relevant phases were derived from a cation-based mineral formula using the stoichiometric method outlined by Schumacher (1991).

5.3 Image Analysis for Feldspar Thermometry

After microprobe analyses of ternary feldspar host and lamellae, a back- scattered electron (BSE) image was taken for image analysis. By image analysis, using the freeware program ImageJ (Rasband, 1997), the proportion of lamellae and host were calculated. The relative proportions are required to obtain the pre-exsolution composition of ternary feldspar, which will be used to determine a temperature by comparison with isotherms obtained from SOLVCALC (section 4.3.1.1). First of all the images were cropped to only display the feldspar grain analysed. Then the image was made binary, turning the plagioclase domain black and the alkali feldspar domain white. Subsequently, an area was selected in which the black pixels, i.e., the percentage of plagioclase, were counted. A representative determination was reached by repeating the pixel counting 5-10 times on slightly different area selections. In general this resulted in a standard deviation of <5%. For calculation of the re-integrated composition, the densities of the plagioclase and alkali feldspar domains are incorporated, 2.67g/cm³ and 2.57g/cm³, respectively (Smith, 1974). The method used for reintegration is sensitive to analytical uncertainties in the analysed feldspar compositions. Benisek et al. (2004) estimated the uncertainties of the calculated temperatures has not been determined, but is assumed to be less than 20°C.

5.4 Whole Rock Sample Preparation

5.4.1 Coarse processing

For XRF analyses and Fe(II) titration on whole rock bulk compositions, and LA-ICP-MS analyses on zircons, coarse processing of eight whole rock samples was carried out at the Geological Technical Laboratory, VU University Amsterdam. First, weathered rims and other parts were removed with a diamond blade saw. A representative part of each rock was selected, as many samples were heterogeneous. For the modelling study it was decided that melanosome and leucosome domains should be separated, if possible, and that only the melanosome part would be used for analysis. However, in some cases leucosome parts could not be fully removed and, in other cases the leucosome and melanosome were mixed at a fine scale. Therefore, it will be indicated which subsamples represent (mainly) the melanosome and which the whole sample. The selected pieces were dried in an oven at \sim 50°C. A steel jaw crusher was used to crush the dry pieces to rock fragments of 2-10 mm in diameter. Contamination from steel and from previous samples was prevented by thorough cleaning of the equipment after each run using a steel brush, compressed air and ethanol. From the crushed material a split of ~100 g was taken for grinding. First, with an agate ring mill for 60 seconds, and subsequently with a planetary mill in an agate pot with agate balls for 60 minutes. This ensures effective grain size reduction and sample homogenisation while the usage of agate keeps contamination to a minimum. Between the processing of samples, the ring and planetary mills were vacuumed, run with quartz sand, rinsed thoroughly with de-mineralized water, and dried with ethanol. After this procedure, a final product of $<70 \ \mu m$ and on average 5 μm in grain size was obtained. Finally, the fine rock powder was put in an open glass tube and dried for one night at ~110°C in a stove, to remove excess water, and afterwards stored in a dehumidifier before further processing (see section 5.4.2). A potential problem during this process was the use of the jaw crusher because of possible metal contamination from the steel blades. However, before Fe(II) titration attention was paid to the possible presence of pure iron. No evidence of the presence of such particles could be found.

For the samples selected for zircon U-Pb dating, a representative aliquot of ~100 g was powdered, as described above, for XRF analysis. The remaining part of the 2-10 mm rock fragments were crushed to <250 μ m. For this, rock fragments were passed through the jaw crusher set at a tighter position, followed by processing in a hardened steel disc mill, which was once set at 500 μ m and twice at 250 μ m. In between each cycle, samples were sieved to withdraw the fraction of <250 μ m. The fraction coarser than 250 μ m was subsequently passed through the disc mill again. Further processing for zircon analysis will be described in sub-section 5.6.2.1.

5.4.2 Preparation of XRF beads

Fused glass beads were prepared for major element analysis by XRF. The first step was to put approximately 1.5 gram of fine whole rock sample powder, produced as described in section 5.4.1, in an oven at 1000°C for 30 min to remove any lattice-bound volatiles such as OH-groups, carbon and sulphur. The relative change of mass during this process, known as the Loss on Ignition (LOI), was determined for each sample by weighing before and after ignition. The LOI generally represents the wt% of volatiles in the sample minus the amount of oxygen taken up by oxidation of FeO. The ignited powder was cooled for ~45 min in a 110°C stove and subsequently put in an airtight glass cabinet to avoid uptake of any water from air. After cooling, 1.000 g of ignited sample was mixed with 4.000 g flux, Spectroflux 110, which consists of 50% lithiummetaborate and 50% lithiumtetraborate. Flux is used because it significantly reduces the melting temperature and so allows melting of sample powder at relative low temperature. The last procedure step was to homogenise the mixture and transfer it into a clean platinum crucible which was placed into a Philips Switch PerIX3 apparatus. An automatic programme melted the material at 1150°C into a bead. Occasionally, the fused beads cracked during cooling upon which the procedure in

the Switch PerIX3 was repeated. Before preparation of another bead, crucibles were cleaned in an ultrasonic bath filled with 20% citric acid for at least 10 min after which they were rinsed with demineralised water and ethanol.

5.5 Whole Rock Analytical Methods

5.5.1 X-ray fluorescence analysis

X-ray fluorescence (XRF) analysis is a type of analytical technique that relies on the unique atomic structure and hence characteristic x-rays of an element (Rollinson, 1993; Winter, 2001). It is typically used for bulk composition measurements (Fitton, 1997) and can detect many elements in concentrations down to a few parts per million (Rollison, 1993; Winter, 2001; Janssens & Van Grieken, 2004). Interference corrected spectra intensities are converted to concentrations against a calibration curve. Element concentrations of internal and external rock standards are monitored for calibration (La Tour, 1989; Janssens & Van Grieken, 2004).

For this study major element concentrations were determined by analysing fused glass beads with a (modified) Philips PANalytical MagiX Pro PW-2540 X-ray fluorescence (XRF) spectrometer at the VU University Amsterdam. An acceleration voltage of 40 kV and a beam current of 90 mA were used to analyse the glass beads. Major elements analysed are: Si, Ti, Al, Fe, Mn, Mg, Ca, K, Na, Ba and P, which are expressed as weight percent (wt%) of the oxides (i.e., SiO₂, Al₂O₃). For each analysis session USGS standards, AGV-1, BCR-2, BHVO-2 and GSP-1 (Raczek et al., 2001), were used as external standards, to check the precision, accuracy and long-term reproducibility of the spectrometer. Table 5.3 provides the average SiO₂, Fe₂O₃, MgO and K₂O concentrations with standard deviations, the relative standard deviation (RSD) and deviation from USGS recommended values over the last nine years. Except for MgO, the precision of XRF analysis, indicated by the RSD, is better than 0.5% (2σ). The accuracy, given as deviation from recommended values, ranges from -4.28% to 1.68%.

5.5.2 Fe(II) Titration

De Roever et al. (2003) have shown that the BGB witnessed oxidising conditions during granulite-facies metamorphism, implying that significant ferric iron (Fe^{3+}) may be incorporated into the structure of the main UHT minerals. As this study initially would involve thermodynamic modelling, and ferric iron is

	AGV-1 (n=64)				GSP-1 (n=62)			
	SiO ₂	Fe_2O_3	MgO	K ₂ O	SiO ₂	Fe ₂ O ₃	MgO	K ₂ O
Average (wt%)	59.68	6.77	1.46	2.97	67.02	4.27	0.94	5.58
Standard deviation 2σ	0.76	0.08	0.04	0.05	0.80	0.05	0.03	0.06
RSD (%) 2σ	1.27	1.22	2.96	1.62	1.20	1.14	3.02	1.13
deviation from recomm. (%)	1.43	0.02	-4.28	1.68	-0.30	-1.86	-3.72	-0.27
	BHVO-2 (r	n=63)			BCR-2 (n=63)			
	SiO ₂	Fe_2O_3	MgO	K ₂ O	SiO ₂	Fe ₂ O ₃	MgO	K ₂ O
Average (wt%)	48.92	12.10	7.04	0.51	53.52	13.59	3.48	1.76
Standard deviation 2σ	0.62	0.19	0.14	0.01	0.77	0.22	0.09	0.03
RSD (%) 2σ	1.27	1.55	1.92	1.36	1.44	1.60	2.64	1.53
deviation from recomm. (%)	-1.41	-1.05	-2.10	-0.40	-1.07	-1.53	-3.03	-1.43

Table 5.3 Reproducibility of a selection of major elements in external standards as measured with the XRF at the VUUniversity Amsterdam over the last nine years.

RSD - relative standard deviation

known to influence the stability field of these minerals (e.g., Harley, 1998a, 2008; Diener & Powell, 2010), it is required to determine the Fe^{2+} and Fe^{3+} levels of the whole rock samples investigated.

The total iron content was determined by XRF analysis. In order to determine how much of the total iron consists of FeO, the method of Yokoyama & Nakamura (2002) was applied. This method is based on Wilson's procedure (1955) in which FeO is analysed by titration of ferrous iron (Fe²⁺). Yokoyama & Nakamura (2002) re-evaluated the method of Wilson's (1955) and developed a more accurate method while overcoming some problems that occurred in previous studies (e.g., Whipple, 1974). Excess V⁵⁺ is added to the sample before decomposition. The following reversible reaction will then occur:

$$Fe^{2+} + V^{5+} = Fe^{3+} + V^{4+}$$

At high acidity this reaction will proceed to the right side and excess V^{5+} will react with all Fe²⁺ present in the silicate sample. The amount of V^{5+} reduced to V^{4+} is then equal to the amount of Fe²⁺ in the sample. Because V^{4+} is extremely resistant to oxidation and does not back-react to V^{5+} during the analytical procedure, the Fe²⁺ concentration in the sample can be determined by measuring the unreacted V^{5+} . This is done by adding excess Fe²⁺ after sample decomposition and subsequently titrating the unreacted Fe²⁺ with Cr⁶⁺. The original FeO content can then be calculated using the following equation:

FeO (wt%)=
$$\frac{(V_{cr} \cdot C_{cr} + W_V \cdot C_V - W_{Fe} \cdot C_{Fe}) \cdot 10^{-3}}{W_{sample}} \times 71.85 \times 100$$

where V_{Cr} is the amount of titrant (mL); W_V , W_{Fe} , and W_{samp} the weights of the V⁵⁺ solution, Fe²⁺ solution, and sample, respectively (g); C_{Cr} is the normality of the titrant (N); and C_V and C_{Fe} the molar concentrations of V⁵⁺ and Fe²⁺ solutions, respectively (in mmol/g). The Fe₂O₃ content can be calculated by difference from the total FeO level as determined by XRF.

Titration is an old wet chemical procedure that has been routinely performed in the previous century. Determination of Fe^{2+} or Fe^{3+} has not been performed at the Petrological Department of the VU University for several decades and therefore the method had to be set-up from scratch (Appendix AII).

5.6 U-Pb Zircon Dating by Laser-Ablation-MC-ICP-MS

5.6.1 The U-Pb system

The U-Pb system is of great importance, because, unlike other chronometers, it exploits two independent decay schemes, ²³⁵U to ²⁰⁷Pb and ²³⁸U to ²⁰⁶Pb. The advantage of two independent chronometers in the same mineral is that it is possible to detect open system behaviour such as Pb loss. This contributes to the reliability and precision of age determinations as it can be evaluated whether a number of analyses truly represent a single time of mineral growth. Furthermore, both uranium decay constants are relatively precisely and accurately known (Jaffey et al., 1971). Zircon is a common uranium-bearing accessory mineral and therefore highly suitable for U-Pb geochronology. Data is commonly displayed in a ²⁰⁷Pb/²³⁸U vs. ²⁰⁶Pb/²³⁸U diagram where the points with the same ²⁰⁷Pb/²³⁵U and ²⁰⁶Pb/²³⁸U age define the concordia line (Wetherill, 1956). In the diagram, the ²⁰⁷Pb/²⁰⁶Pb age is represented by the slope of the line defined by the origin and a point on the concordia.
5.6.2 Zircon separation and preparation

5.6.2.1 Zircon separation from whole rock

After coarse processing, where whole rock samples of ~4 kg or more were reduced to a grain size of less than 250 µm, conventional mineral separation techniques were used at the Mineral Separation Laboratory of the VU University (e.g., Fuerstenau & Han, 2003; Bhagwat, 2009). First, <30µm particles were removed with the aid of a desliming apparatus making use of Stoke's law (e.g., Johnson, 1998). After drying of the deslimed material, the heavy minerals were separated with using heavy liquids. Zircons are among the heaviest minerals (ρ =4.65g/cm³) in the crushed samples and can, therefore, easily be separated. In order to do so, the heavy liquid diiodomethane (ρ =3.34g/cm³) mixed in variable ratios with dichlorobenzene to obtain the desired density, was used in a liquid overflow centrifuge (LOC). Particles will then either float ($\rho_{\text{particle}} < \rho_{\text{liquid}}$) or sink ($\rho_{\text{particle}} > \rho_{\text{liquid}}$). A first step was performed at a fluid density of 2.98g/cm³, and a second step at 3.30g/cm³. The sink was passed through an ore magnet to eliminate the most magnetic fraction, and subsequently sieved to obtain multiple grain size fractions (<90, 90-120, 120-180 and >180 μ m). Finally the grain size fractions were passed through a high-gradient Frantz Isodynamic magnetic separator (e.g., Svoboda, 2004). Zircon grains have by far the lowest magnetic susceptibility of the heavy minerals and are consequently not influenced by the Frantz magnetic field. By progressively increasing the magnetic current after each cycle, final fractions consisting of >99% zircon were obtained. Not only magnetic susceptible minerals were split from zircon grains, but also metamict and cracked zircons were removed because of their slightly higher magnetic susceptibility.

From the zircon mineral concentrate, non-metamict zircons with the least cracks and inclusions were hand-picked with the aid of a stereomicroscope. Around 130 zircons were isolated and sorted into several groups based on crystal form, colour and transparency. Due to the absence of sufficient transparent and/or euhedral zircon crystals, a lot of zircons containing inclusions and/or fractures were selected for sample FN69, a mesoperthite granulite. The selected zircons were mounted in a 25 mm diameter epoxy section, polished and carbon-coated by the Geological Technical Laboratory at VU University Amsterdam.

5.6.2.2 Back-scattered electron images

Cathodoluminescence (CL) microscopy is commonly used to observe variations in luminescence of zircons for LA-ICP-MS analysis, preferably in combination with back-scattered electron images. However, the CL microscope at VU University Amsterdam was out of order during this study and zircons were therefore examined with an electron microprobe instead. Back-scattered electron images were taken



Figure 5.2 Zircon from granodiorite sample FN60 (grain KET1-10). **a.** Back-scattered electron image visualising zircon growth patterns. **b.** Light microscopy image, to characterise the location of inclusions and cracks within a zircon grain.

to visualise zircon growth patterns and the presence of inherited cores (Fig. 5.2a; sample FN60, KET1-10). Light microscopy images were made to determine the location of inclusions and cracks within the zircon grains (Fig. 5.2b). With combined information the best spot location for analysis could be selected, avoiding cracks, inclusions and zones of irregular growth.

5.6.3 Laser Ablation Inductively Coupled Mass Spectrometer

In situ U-Pb isotope data of mounted zircon grains were acquired with a Laser Ablation Inductively Coupled Mass Spectrometer (LA-ICP-MS) at the Faculty of Geosciences, Utrecht University. This is a powerful analytical instrument that enables highly sensitive chemical analysis down to parts per billion levels that can directly be performed on solid samples (Gray, 1985; Sylvester, 2001). The instrument in Utrecht uses an infrared Lambda Physik ArF excimer (193 nm) coupled to a GeoLAS optics system for ablation. Element concentrations of the ablated material were determined with a single collector quadrupole Thermo Finnigan Element-2 ICP-MS. By solely changing the electrical field at a constant magnetic field strength it was possible to measure all masses from ²⁰⁰Hg to ²⁴⁸ThO. All four lead isotopes (²⁰⁴Pb, ²⁰⁵Pb, ²⁰⁵Pb and ²⁰⁸Pb), ²³⁵U and ²³⁸U were measured, with the addition of ²⁰⁰Hg, ²⁰²Hg, ²³²Th and ²⁴⁸Th.

Prior to laser-ablation, zircon zones were selected in the grain core, avoiding cracks and inclusions. Depending on the space available in the grain, laser ablation spots were 30 μ m or 40 μ m in diameter. Analyses were performed on three samples (MKS40, FN60 and FN69) with 37 to 84 individual zircons per sample. Internal zircon standard Z91500 (Yuan et al., 2004; Wiedenbeck et al., 2004) is measured three to four times at the beginning and end of a series of 5-7 sample zircon spots. The standard is analysed with the same spot-size as in the series, as the spot diameter can be of influence on fractionation processes. Internal correction of obtained sample ratios and error calculations are accomplished using this standard bracketing method. Concurrently, this monitors the instrumental drift. Data were acquired during 40 seconds on average, preceded by ~30-45 sec and followed by ~10 sec baseline measurements during which the laser was switched off. Instrument operation parameters used in this study are presented in Table 5.4.

Laser ablation co	nditions	ICP-MS conditions:				
Wavelength:	193 nm	m/∆m	300			
Pulse duration:	5 ns	Plasma power:	1060 W			
Spot diameter:	30-40 μm	Dwell time:	100 ms			
Repetition frequency:	10-15 Hz	Carrier flow rate:	0.90 L/min He			
Power density:	20 J/cm ²	Plasma gas flow rate:	13.5 L/min Ar			
Energy/pulse:	16 mJ					

Table 5.4 Analytical parameters used in this study during LA-ICP-MS analysis.

The LA-ICP-MS has several benefits. For example, no complex and time-consuming sample preparation as needed for solution-ICP-MS techniques. The method also delivers results within minutes and allows analysis of individual grains and even parts of grains. And most important for U-Pb analysis, in which an age resolution of better than 1% is desired, LA-ICP-MS delivers very high quality analyses when the machine is optimally tuned. However, the technique is technically challenging and also has its limitations. Fundamental processes that control the ablation process are highly complex and need to be understood in detail to achieve accurate and precise analytical data. One major subject of concern is that laser-ablation analysis is plagued by mass and elemental fractionation (Yaun et al., 2004; Chang et al., 2006). To achieve high levels of precision accurate correction for these fractionation processes is required (see section 5.6.4). Another main limitation is caused by interference with oxide compounds, matrix elements

and other molecular species. Correction for these interferences is difficult, because the magnitude of specific interferences cannot be determined easily. To keep mass bias to a minimum, the Element-2 ICP-MS is tuned at the start of each measurement day, which at the same time optimises the signal intensity. Oxide interference was monitored at mass 248 (²³²Th¹⁶O) and was found to be insignificant for each session. A reference zircon standard from the petrological department of the VU University Amsterdam, as well as an Archean zircon of rather precisely known U-Pb SHRIMP concordia age have been analysed as external standards (Klaver, *pers comm.*). The obtained U-Pb LA-ICP-MS concordia ages are within error of the published data (Jackson et al., 2004; Thorpe et al., 1992), assuring that the obtained LA-ICP-MS data are highly accurate (Table 5.5).

	data: / ges obta		En lei Mis concordia ages.
External Standard	Age (Ma)	Recomm. value (Ma)	Deviation from recomm. value (%)
GJ-1	610 ± 8	608.5 ± 0.4	-0.20
Jan Wijbrans Archean sample	3465 ± 11	3458 ± 1.9	-0.25
	Parta a state	1	A selection of the second s

Table 5.5 LA-ICP-MS external standard data. Ages obtained for this study are U-Pb LA-ICP-MS concordia ages.

GJ-1 recommended values are U-Pb TIMS concordia ages obtained by Jackson et al. (2004). For the Jan Wijbrans Archaean sample U-Pb SHRIMP concordia ages were obtained by Thorpe et al. (1992).

5.6.4 U-Pb data reduction

The obtained uranium and lead isotopic data were corrected using the open-source program Iolite (Hellstrom et al., 2008). This uses a U-Th-Pb data reduction scheme which is fully discussed by Paton et al. (2010) and will be briefly treated here.

The first step in Iolite is correction for background noise. In order to exclude baseline intensities from sample and standard analyses, values are interpolated between periods of blank measurements using a smoothed spline function. Then baseline-subtracted beam intensities are calculated by subtracting the baseline spline from the raw beam intensity at each data point.

Secondly, with the use of zircon standard Z91500, data are corrected for time-dependant element fractionation, such as laser-induced down-hole elemental fractional and instrumental mass discrimination. This is the most important stage of data reduction and should carefully be performed. First of all, reference standard analyses should manually be selected. Here it is important to note anomalies in signal intensity, which for example may result from surface Pb contamination, cracks in a grain or the laser drilling all the way through a thin part of a grain. After selection, the most appropriate best-fit solution should be chosen, which fits a formula to the data. Iolite provides a number of different model types from which can be chosen, and for this study, an exponential formula fitted best. Once done, the program will apply the derived exponential time-fractionation law to calculate mass-dependent corrected element ratios and drift-corrected elemental and isotopic ratios. The exponential formula did not fit the ²⁰⁸Pb/²³²Th vs. time curve, as it yields a parabolic shape, and, therefore, much less emphasis is placed on geochronological information derived from the thorium-lead decay system in this study. Modelling and correction of time-dependent elemental fractionation is carried out before correction of long-term instrumental drift in isotopic or elemental ratios. To correct for this static fractionation, normalisation to the reference standard Z91500 is applied to all ratios (i.e., sample-standard bracketing).

Finally, the optimal regions of sample analyses should be selected for export. For each analysis run the first few seconds of collection are excluded to preclude any surface contamination and avoid inclusion of the released thin carbon layer during the first few laser pulses. Additionally, anomalies in beam

intensity are left out. At the end, when data processing is complete, a table of results can be exported from Iolite. This step includes propagation of uncertainties and calculation of error correlations.

After the final data has been exported, further filtering is required, excluding certain analyses. To avoid non-representative data, analyses with a collection time of less than 20 seconds were not taken into account. A problematic factor is the presence of common lead. ²⁰⁴Pb can be used to monitor the contribution of common lead, but is affected by isobaric interferences of ²⁰⁴Hg, introducing another correction factor. However, only when all analyses contain significant amounts of common lead (final ²⁰⁶Pb/²⁰⁴Pb ratio <10,000), correction is necessary. If ²⁰⁴Pb intensities are very low and indistinguishable from blank measurements, correction for common lead would only introduce an additional, larger error. A few analyses of sample FN60 contained a final ²⁰⁶Pb/²⁰⁴Pb ratio of less than 10,000, but did not show any signal intensity other than blank intensities in the raw ICP-MS data. The decision was made to discard the analysis with very low ²⁰⁶Pb/²⁰⁴Pb ratio, of <2,500, without applying an additional correction. As mentioned, oxide interferences during analysis were found to be insignificant and can be neglected.

6. FIELD OBSERVATIONS AND PETROGRAPHY

Lenses of pelitic gneiss that occur throughout a large part of the Bakhuis Granulite Belt were the primary targets for fieldwork. In addition, three known occurrences of mesoperthite granulite were inspected. Samples were gathered along the Lower Fallawatra River, the Nickerie River near the Blanche Marie Falls, the Vanamkreek, the Kabalebo River up- and downstream relative to Kabalebo Nature Resort, and the Zandkreek (Fig. 6.1). As mentioned in section 5.1.1, the jungle prevented systematic inspection of field relationships. This study, however, does not require a good comprehension of the relations between rock types, as its importance lies in the mineralogy of rock samples. A total of 41 samples from 24 sample locations have been microscopically examined. Furthermore, 37 samples from old collections and previous fieldwork have been studied. Mineral abbreviations follow Whitney & Evans (2010).

6.1 Pelitic Gneiss

Pelitic gneisses are generally exposed as relatively small, isolated outcrops of 4-8 m² along rivers or creeks (Fig. 6.2a), and more rarely as metre-sized blocks in the jungle near creeks. Most outcrops are partly weathered and covered with different kinds of lichen, giving a green, black, or orange appearance (Fig. 6.2b). Below the river waterline rocks are usually covered by a thin black deposit. In the field metapelitic rocks display fine, discontinuous compositional banding, which is different from the continuous and wider banding of the granulites. The fine banding represents small-scale segregation into melanosomes and leucosomes (Fig. 6.2c). The melanosomes are primarily composed of sil + bt \pm crd, in some cases with grt and rarely with opx. Except for cordierite, these minerals are recognisable in the field. The grain size is intermediate to coarse (1-8 mm) and the texture typically gneissose with foliation by bt and sil. Apart from fine, discontinuous leucosome layers (mm scale), also wider and continuous leucosome parts have a higher resistance to weathering compared to the melanosome, and consequently often stand out on exposed surfaces giving a finely banded pattern to the outcrops (Fig. 6.2b). The banding and foliation are often steeply to rather steeply oriented. Locally, folding of layers is observed, with a steeply inclined fold axis.

Light microscopy shows that the pelitic gneisses are characterised by a mineral assemblage of sil + $qz + fsp + bt \pm crd$ with zircon, opaque minerals and green spinel as common accessory minerals. In some



Figure 6.2 Characteristic pelitic gneiss. **a.** Typical outcrop along a creek (Vanamkreek; sample location FN42). **b.** Compositional layering with quartz lens (outcrop sample FN04; Fallawatra River). **c.** Thin-section (26 mm in width), showing two distinct layers, melanosome and leucosome (sample FN35).



Figure 6.1 Schematic map of the Bakhuis Granulite Belt (after de Roever et al., 2003; see Fig. 3.4), displaying GPS determined sample locations marked by red and blue circles. **Upper map.** Samples collected during fieldwork in 2012. **Lower map.** Samples collected by E. de Roever in 1977 at GMD and during fieldwork in 2010 - 2012. LE - LE34.1; LA - LA156 6.5, LA158.17, LA162.7; LJ2 - LJ2 30.0, LJ2 40.0A, LJ2 40.3; IV - IV894, IV900, IV901.

samples additional grt, opx, crn, ky and very rarely spr were found. The minerals are evidently not in equilibrium with each other, as is shown by differences in grain-size and mode of occurrence. Cordierite, grt, part of sil and bt, and opx form comparatively large crystals, whereas ky and part of sil and bt form fine-grained aggregrates, which are at least in part pseudomorphs after cordierite. A map of the distribution of characteristic UHT minerals is provided in the Chapter 8.

Cordierite - Cordierite can easily be recognised by the presence of simple lamellar twinning (Fig. 6.3b), together with partial replacement along its rims, into fine-grained sil and bt. In some samples (e.g., FN72, FN86) the rims of recrystallisation products are narrow, only ~0.1 mm. However, in many rocks cordierite is largely or fully replaced, by aggregates of fine-grained sil, bt and opx (Fig. 6.3a). Fine-grained kyanite is also found in part of the pseudomorphs after cordierite, usually in association with much biotite. Recognition of such fine-grained pseudomorphs may be difficult, especially in deformed rocks, but in many cases remnants of cordierite are present locally. Cordierite was not found in the Fallawatra area, where opx + sil + qz and spr ± qz have been found. However, outside this area rather abundant cordierite or its pseudomorphs have been observed at all locations sampled and in most of the metapelite samples, accompanied by coarse sillimanite. Its relations to the characteristic peak metamorphic mineral orthopyroxene could be established in samples with less retrograde metamorphism, such as the drill core samples LJ2 in the SW of the belt. Some of these samples contain large intergrown crystals of opx and crd.

Sillimanite - In samples with sillimanite two generations can usually be distinguished. The older generation is characterised by a coarse grain size (Fig. 6.3c) of 2 mm on average and up to 1 cm in length. The coarse generation is considered to represent the peak metamorphic stage. Coarse sillimanite usually shows reddish zones composed of many tiny inclusions of reddish opaque material (Fig. 6.3c), which are interpreted to have formed by exsolution after peak metamorphism. Sillimanite grains are often oriented parallel to the foliation. The younger generation consists of a much finer population which formed as a retrograde product that partly or fully replaced original peak metamorphic grains. Fine acicular sillimanite is dominantly observed in combination with fine to very fine-grained biotite and opaque minerals and/or fine to very fine orthopyroxene, as pseudomorphs after cordierite and as rims at the borders of coarse sil and opx.

Orthopyroxene - Orthopyroxene is relatively rare and was found mainly at two locations in the SW of the BGB and in the Fallawatra occurrence. In opx-bearing samples two generations can be distinguished in many cases. The older generation is characterised by a coarse grain size (Fig. 6.3d) of 2 mm on average and ranges up to even 25 mm. This generation is considered to represent the peak metamorphic stage. Coarse orthopyroxene usually contains many tiny dark brown to red square patches (Fig. 6.3d), which are interpreted to have formed by exsolution after peak metamorphism. The coarse opx grains can easily be recognised by their clear or more subtle pink to mint-green pleochroism. Cleavage is rather poorly developed and crystals may have an anhedral, equidimensional habit. The younger generation consists of a very fine population which clearly formed as a retrograde product that partly or fully replaced the original peak metamorphic grains. Fine to very fine orthopyroxene grains are common in pseudomorphs after cordierite and, in cases, occur with other reaction products around coarse orthopyroxene. The retrograde metamorphism of coarse orthopyroxene appears to be less in felsic parts, probably because qz and fsp grains formed a buffer against post-peak reactions.

Next page - Figure 6.3 Thin section microphotographs of typical mineral occurrences in Bakhuis Granulite Belt metapelitic rocks. **a.** Plane polarised light (PPL), coarse sillimanite (centre) surrounded by biotite and sapphirine (sample LJ2 40.4). **b.** PPL, coarse orthopyroxene (centre) with brown patches (sample IV901). **c.** PPL, cordierite (centre) with fine acicular recrystallisation products at its rims (sample FN05). **d.** XPL, the same as c), note the characteristic twinning. **e.** PPL, secondary garnet enclosing fine biotite, sillimanite and opaque minerals (sample FN36). **f.** XPL, the same as e. **g.** PPL, poikiloblastic sapphirine (centre) with feldspar inclusions, surrounded by biotite and opaque minerals (sample LJ2 40.4). **h.** XPL, the same as g), possibly in contact with quartz in the left corner.



Sapphirine - Sapphirine occurs in small amounts in many metapelitic rocks of the Fallawatra occurence (de Groot, 2008). It occurs here as egg-shaped grains included in fsp and sil and, occasionally, in garnet (Fig. 6.4). Outside this area it was only found as secondary sapphirine in symplectic spr-crd intergrowths at two locations in the SW. Therefore, the discovery of abundant primary sapphirine in a drill-core (core LJ2) in the SW of the belt is exceptional. The sapphirine occurs in a narrow layer and covers ~30% of the thin-section (Fig. 6.5). It was not found in direct contact with quartz, but occurs in a quartz-rich layer and most probably formed in stable coexistence with quartz. The sapphirine shows a striking blue to blue-green pleochroism and occurs in this layer mainly as anhedral poikiloblasts with fine feldspar inclusions (Fig. 6.3e,f). It is closely associated with sillimanite, biotite and opaque minerals and in part forms intergrowths with relatively coarse sillimanite.

Garnet - Garnet is an important constituent of many high-grade metamorphic terranes, but is less common in the BGB. The main type found is poikiloblastic garnet enclosing fine-grained sil, bt, qz and/or opaque minerals (Fig. 6.3g,h). Based on the assumption that fine inclusions of sil and bt represent retrograde products of e.g., cordierite, the poikiloblastic garnet is considered to be clearly not coeval with the peak metamorphic minerals. It most likely represents a relatively young stage of the retrograde path. Another form of garnet is rarely observed. It does not contain fine-grained inclusions of retrograde products but rather coarse inclusions of spr and opx (Fig. 6.4). These garnet crystals have formed at the expense of orthopyroxene and sapphirine, but may have formed initially in equilibrium with these minerals.

Biotite - Biotite shows a striking reddish-brown pleochroism and commonly appears in fine- grained retrograde masses. It also occurs as sub- to euhedral crystals as large as 4 mm in size, of uncertain generation.

Corundum - In several metapelite samples corundum was found (e.g., LJ2 40.3) which is remarkable because of the considerable level of quartz in these rocks. Corundum stands out by its euhedral prismatic habit, high relief and fracturing instead of cleavage (Fig. 6.6). It occurs as medium-sized grains of ~1 mm in size, and is mostly associated with opaque mineral grains of similar size, but is in rare cases nearly free of opaque minerals. The intergrowth with opaque oxides indicates that crn presumably formed by exsolution from a high-temperature spinel solid solution. The association of crn + qtz thus not necessarily was not necessarily formed in equilibrium with each other.



Figure 6.4 PPL of coarse garnet with sapphirine inclusions (sample VG80).



Figure 6.5 Transmitted light photograph of a metapelitic rock (sample LJ 2 40.4; 27 mm in width).



Figure 6.6 PPL, aggregate of coarse corundum crystal (centre) associated with opaque minerals (sample LJ2 40.3).



Figure 6.7 Exsolved ternary feldspar grains (sample MKS40D, metapelite). **a.** Mesoperthite with exsolution in blocky patches. **b.** Mesoperthite with fine (left) and coarse (right) lamellae (sample ER23A, granulite).

Quartz - Quartz generally exhibits medium-sized anhedral grains (~2 mm) and frequently encloses tiny needle-like mineral inclusions giving a blue greyish luster in hand specimen. The quartz grains are partly affected by deformation as indicated by undulose extinction, microdomains, and recrystallisation into fine grains (<0.1 mm).

Feldspar - Plagioclase is the dominant feldspar and is in many cases accompanied by K-feldspar. Feldspar grains are in general anhedral and have an overall size of around 1-3 mm but can reach up to 15 mm in length. Feldspar exsolution is very common and, as partly illustrated in Figure 6.7, there is a wide variety of unmixing with percentages ranging from 10% (antiperthite, perthite) to 50% (mesoperthite). Several exsolution textures occur, such as blocky patches, vermicular forms, and laminated textures. Lamellae range in width from coarse, up to 50 μ m, to fine, micrometer-sized. Plagioclase grains with 10-20% blocky patches of K-feldspar are common, but non-exsolved plagioclase grains are abundant, as well. Mesoperthite is the dominant feldspar in a number of samples, such as RG 1508. In other samples, such as MKS 40, large, mm-sized mesoperthite grains occur in a fine-grained mass of plagioclase and perthite. The coarse mesoperthite is assumed to have formed during peak metamorphism, whilst the fine grains are recrystallised from the break-down product of coarse mesoperthite during a retrograde stage of metamorphism.

Opaque minerals - Opaque minerals are common in pelitic gneisses of the BGB and may form coarse aggregates between (coarse) opx and sil, commonly with inclusions of green spinel. They are dominantly primary, but may also have a secondary origin, e.g., as fine grains associated with other fine minerals around peak-metamorphic minerals such as coarse sillimanite. Another fairly common accessory mineral is zircon.

Graphite - Graphite was found in rather small amount in a drill core (LA162.7). It can be recognised by its tabular crystal shape and intense black colour in PPL and XPL. In the drill core graphite was associated with grt and some opx.

6.2 Mesoperthite Granulite

In the past mesoperthite granulite has been found at rather many isolated occurrences in the Bakhuis Granulite Belt, surrounded by banded granulites. During the 2012 fieldwork, only a few localities of mesoperthite granulite could be reached and sampled. One outcrop within the Kabalebo River was completely flooded, but samples could be taken on the river bank (FN47 and FN69; Fig. 6.8a). The mesoperthite-bearing samples taken in 2009 (ER23A-D) appear to indicate that the mesoperthite granulite occurrence is as wide as the river, in the order of 20 m. Another occurrence along the Kabalebo River was



Figure 6.8 Mesoperthite granulite characteristics. **a.** Outcrop of rather homogeneous mesoperthite granulite along the Kabalebo River (sample location FN69). **b.** Sawed section of granulite (sample FN45B).

also beneath the waterline, but samples could be taken 500 m inland (FN66). The size of that occurrence could not be estimated. Along the Vanamkreek mesoperthite granulite had been sampled in the 1960s (GF348), together with other granulites. During fieldwork in February 2012 an outcrop of leucocratic granulite with a width in the order of 10 m was found between banded granulites. The sample taken (FN45) did not contain mesoperthite but abundant perthite and antiperthite. Mesoperthite granulites were not thoroughly examined in previous studies and therefore one large sample, FN69, was collected along the Kabelebo River for XRF bulk rock composition and U-Pb zircon geochronology.

Mesoperthite granulite outcrops have a rather homogeneous appearance. They are quite leucocratic in hand specimen, consisting nearly entirely of qz and fsp. Besides abundant qz and fsp minor amounts of biotite, opaque minerals and zircon are present in the granulite. In some samples small amounts of opx and/or grt are found. The orthopyroxene is anhedral, up to ½ mm in grain size and is highly altered. Generally, qz and fsp are medium grained (1-5 mm) and proportionated to approximately 40% and 60%, respectively. Quartz has an anhedral habit, and commonly shows effects of deformation. In cases, parallel quartz lenses occur, giving a crude foliation to the rocks (Fig. 6.8b). Feldspar comprises mesoperthite with some antiperthite and perthite (Fig. 6.7).

6.3 Sillimanite-cordierite Granodiorite

According to the 1978 geological map a small zone of metapelite is present along the upstream part of the Zandkreek, a major tributary of the Kabalebo River that extends southwards deep into the central part of the BGB. The location has been sampled previously by E. de Roever and was revisited because of its peculiar characteristics, such as a considerable amount of sil and crd, suggesting a metapelitic origin. In the field the rocks are massive and homogeneous, resembling magmatic rocks. This appearance is rather similar to nearby charnockites along the Zandkreek and entirely different from finely banded pelitic gneisses. Some vague banding could be observed, which is also observed in charnockites. A striking characteristic of the rocks was the presence of several xenoliths with angular shape and variable size from a few cm to 70 cm (Fig. 6.9). The xenoliths consist of fairly fine metadoleritic rock. Such xenoliths are quite common in charnockites in the SW of the belt (Klaver, 2011). A large sample (FN60) was taken for XRF analysis and zircon geochronology in order to determine whether the rock might be related to the surrounding charnockites.



Figure 6.9 Sillimanite-cordierite granodiorite field appearances (sample location FN60). **a.** Homogeneous outcrop in the middle of the Zand Creek **b.** Angular large mafic xenolith (70 x 50 cm; sample FN58). **c.** Medium sized angular mafic xenolith (12 x 10 cm; sample FN59).

Sample FN60 consists mainly of pl, kfs and qz, with roughly 10% bt, 5% sil, 3% crd and 10% opaque minerals. The sample is highly mylonitised with plagioclase as large porphyroclasts, up to 2 cm, which have not been broken up by the deformation. Generally, the plagioclase is not exsolved. Quartz has deformed and recrystallised into very fine grains of <0.01 mm, and alternates with layers of biotite and other fine material that bend around coarse plagioclase porphyroclasts (Fig. 6.10). Cordierite grains show borders of fine reaction products. Thin-section FN60B also contains two grains of garnet (~1 mm) which are brecciated and partly recrystallised. The rock is not a charnockite, because it does not contain orthopyroxene, and is, therefore, called a sillimanite-cordierite granodiorite.



Figure 6.10 Sample FN60B: sillimanite-cordierite granodiorite. a. Transmitted light photograph of thin section (27 mm in width; ~150 mu). b. PPL, feldspar porphyroclast within mylonitised structure. c. XPL, same as b). Note the fine recrystallised quartz grains.

7. ANALYTICAL RESULTS

7.1 Ternary Feldspar

7.1.1 Feldspar mineral composition

Figure 7.1 displays the compositional variation in exsolved feldspar components, K-feldspar (blue circles) and plagioclase (green circles), with the integrated ternary feldspar composition in between (red circles). The composition of the exsolved K-feldspar domains vary over the range Or_{0.854-0.964} Ab_{0.139-0.034} Exsolved plagioclase An_{0.009-0.000}. domains show а much broader compositional range from An_{0.373} to $An_{0.074}$, with the orthoclase component in general <0.01. Re-integrated feldspar differ considerably compositions in composition, depending on the texture of the grains (i.e., antiperthitic, mesoperthitic, Table perthitic). 7.1 provides representative compositions of all textural forms. Overall, the anorthite component is lower than 29% and the albite content >17%. The BaO and SrO components in re-integrated feldspar are <0.23wt% and <0.35wt%, respectively.



Figure 7.1 An-Ab-Or ternary diagram with exsolved (K-feldspar – blue; plagioclase – green) and re-integrated feldspar compositions (red circles) for all analysed samples. Solvus curves are calculated for 800-1100°C at 0.85GPa using the model of Fuhrman & Lindsley (1988). An – anorthite; Ab – albite; Or – orthoclase.

7.1.2 Feldspar thermometry

Feldspar thermometry has been applied to a selection of samples spread throughout the whole Bakhuis Granulite Belt. Figure 7.2 provides ternary plots with re-integrated feldspar compositions of all analysed samples along with solvus curves for 800-1100°C calculated at 0.85 GPa using the model of Fuhrman & Lindsley (1988). Most data points plot between the 900°C and 1000°C isotherms, with some perthite and antiperthite grains plotting below 900°C. The celsian component (BaAl₂Si₂O₈) in re-integrated feldspar compositions is <1%, which would generate less than 1°C fluctuation (e.g., Jiao & Guo, 2011). Therefore, the celsian content was disregarded for temperature determinations. The same holds for the very low Sr level of re-integrated feldspars.

The representative feldspar temperature for a specific sample is not necessarily the average temperature of all analysed grains within that sample. The temperature adopted depends on the exsolution type of the grains. As visualised in Figure 7.3, several textures can be recognised: M, M^* , A and P. In samples such as RG1508 and IV894, all analysed grains are mesoperthitic and the re-integrated compositions plot in a cluster (M; Fig. 7.3a). For those samples an average temperature is taken. Other samples, such as ER23A and SA714, contain mesoperthitic feldspars that vary in re-integrated composition, but plot approximately on the same isotherm (M^* ; Fig. 7.3b). Also here an average of the temperatures is taken. Although the sample selection was aimed at mesoperthite, many samples do not contain mesoperthite and, therefore, antiperthite (A) with significant exsolution and, in cases, perthite (P) grains had to be selected. Some samples include both A and P (Figure 7.3c). In these samples re-

wineral	Feidspar									
Sample	FN43 - fsp	6		FN52 – fsp2	2		RG1508 - fsp1			
Texture	antiperthi	tic fsp		perthitic fs	0		mesoper	mesoperthitic fsp		
Domain	host	lamellae	reint.	lamellae	host	reint.	*	*	reint.	
wt%	(PI)	(Kfs)		(PI)	(Kfs)		(PI)	(Kfs)		
SiO ₂	62.02	64.12	62.35	64.58	64.79	64.72	60.70	64.45	62.47	
AI_2O_3	23.42	18.33	22.63	22.22	18.60	19.75	24.30	18.39	21.51	
CaO	5.24	0.06	4.44	4.20	0.19	1.47	5.95	0.13	3.20	
Na ₂ O	8.97	1.39	7.80	8.76	2.44	4.45	7.96	1.04	4.69	
K ₂ O	0.17	14.89	2.44	0.16	13.16	9.02	0.14	15.16	7.23	
BaO	0.01	0.50	0.08	0.00	0.41	0.28	0.00	0.48	0.23	
SrO	0.34	0.42	0.35	0.44	0.31	0.35	0.10	0.13	0.12	
Total	100.16	99.72	100.09	100.34	99.90	100.04	99.14	99.78	99.44	
Normalised to	o 5 cations									
Si	2.74	2.97	2.78	2.87	2.98	2.94	2.73	2.99	2.85	
Al	1.22	1.00	1.19	1.16	1.01	1.06	1.29	1.00	1.16	
Са	0.25	0.00	0.21	0.20	0.01	0.07	0.29	0.01	0.16	
Na	0.77	0.13	0.67	0.75	0.22	0.39	0.69	0.09	0.41	
К	0.01	0.88	0.14	0.01	0.77	0.52	0.01	0.90	0.42	
Ва	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.00	
Sr	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	
weight prop.	0.85	0.15		0.32	0.68		0.47	0.53		
An	0.242	0.003	0.207	0.163	0.004	0.041	0.290	0.006	0.158	
Ab	0.749	0.124	0.658	0.827	0.108	0.278	0.702	0.094	0.418	
Or	0.009	0.873	0.136	0.010	0.888	0.681	0.008	0.900	0.424	
FL(88) (°C)			864			863			1055	

Table 7.1 Representative ternary feldspar compositions.

* no host and lamellae could be distinguished.

fsp – feldspar; reint. – reintegrated; pl – plagioclase; kfs – K-feldspar; weight prop. – weight proportion based on image analysis and domain density; FL(88) – temperatures are graphically determined using the model of Fuhrman & Lindsley (1988).

integrated *P* compositions systematically give a lower temperature than *A* grains. Therefore, for those samples only the results of *A* grains are taken into account. Contrary to samples with antiperthite accompanied by perthite, antiperthite without associated perthite does not need to contain a high potassium level and, therefore, might record a fairly low temperature. Samples containing only *A* grains display a trend from lower Or content towards higher Or in the re-integrated composition (FN43; Fig. 7.3d). The most Or-rich composition represents the nearest approximation of antiperthite exsolution and is, therefore, selected as representative for thermometry. Some samples only contain perthite as main exsolved feldspar (Fig. 7.3e). As displayed in Figure 7.3c, perthite grains yield systematically lower

Table 7.2 Feldspar thermometr	y temperatures.
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	Rock					Rock			Temperature
Sample	type	Texture	n	Temperature (°C)	Sample	type	Texture	n	(°C)
AB447	Мр	Α		941	JJ337	Мр	М*	6	926 (9)
ER23A	Mgr	М*	7	979 (6)	KG984	Мр	М*	5	919 (1)
FN28	Мр	Α		970	LA156 6.5	lg	Α		986
FN43	Мр	Α		940	LA158.17	lg	Α		1012
FN45A	Mgr	Α		970	LE34.1	lg	Α		918
FN45B	Mgr	Ρ		896	LJ2 40.0A	Мр	М	5	986 (6)
FN47B	Mgr	M*	5	977 (20)	MKS 40D	Мр	A(M)		1042
FN52	Мр	Ρ		955	RG1508	Мр	М	4	1047 (8)
GF348	Mgr	M*	4	978 (3)	SA714	Мр	М*	5	901 (9)
IV894	Мр	М	3	1003 (3)	SA776	Мр	М	4	999 (10)

Numbers in parentheses indicate one standard deviation (1σ) in terms of last significant numbers: 979(6) should be read as 979 ± 6. *n* – number of analyses; *A* – antiperthic feldspar; *M* – mesoperthitic feldspar; *M** - mesoperthitic feldspar plotting along a single isotherm; *P* – perthitic feldspar.



Figure 7.2 Detailed ternary plots of re-integrated feldspar compositions of all analysed Bakhuis Granulite Bakhuis samples. Solvus curves are calculated for 800-1100°C at 0.85GPa using the model of Fuhrman & Lindsley (1988).



Figure 7.3 Ternary feldspar diagrams, displaying different textural feldspar types. Included is a selection of representative re-integrated feldspar compositions. Solvus curves are calculated for 800-1100°C at 0.85GPa using the model of Fuhrman & Lindsley (1988). **a.** M -mesoperthite; **b.** M^* - mesoperthite on an isotherm. **c.** A + P - antiperthite and perthite. **d.** A - antiperthite. Note the trend towards an Or-poor composition. **e.** P - perthite.

temperatures than A grains in samples with both A and P. However, for sample FN52 no other markedly exsolved feldspar than perthite was available for analysis. The most An-rich grain is selected as representative of peak metamorphism. Also sample FN45B only contains P grains, but is taken from the same hand specimen as FN45A which includes A grains (Fig. 7.3.e). These A grains yield higher temperatures for feldspar grains present only 10 cm from the P grains in FN45B. Once more, this supports that P grains should only be taken into consideration for feldspar thermometry if no other option is available. Finally, there is one sample, KG984, for which distinct ternary fsp types are analysed. As expected from the previous discussion, the antiperthite and perthite grains yield lower temperatures and the mesoperthite grains the highest. Both mesoperthite grains lie nearly on the same isotherm and an average of these two temperatures is taken. In Table 7.2 the representative temperatures are given, with an indication of the texture as discussed above. The temperature of each individual reintegrated grain can be found in Appendix A.III.1 together with a BSE image. The highest temperature (1047°C) is recorded by mesoperthite in sample RG1508, which shows evenly spaced exsolution lamellae and rods. Except for perthite in sample FN45B the selected temperatures are above 900°C and range up to 1047°C. In the discussion, the highest temperature has been selected for samples from the same location.

7.2 Mineral Chemistry

The parameter X_{Mg^*} represents Mg/(Fe²⁺ + Mg) for analyses for which the Fe³⁺ content was calculated on the base of mineral stoichiometry. X_{Mg} represents Mg/(Fe^{tot} + Mg) with Fe as total iron. Representative mineral analyses are given in Table 7. Appendix A.III.2 provides all data.

Orthopyroxene - Orthopyroxene in pelitic gneisses from outside the Fallawatra occurrence is characterised by a high Al₂O₃ content ranging from 6.0 - 8.7wt%. All analysed orthopyroxenes are in coexistence with Al-rich phases, sillimanite and/or cordierite. Zoning is common (Table 7.3). The rim is less aluminous, with up to 1.6wt% Al₂O₃ less than in the core. While Al decreases towards the rim the XMg* ratio remains almost constant (Fig. 7.4). Zoning in Al₂O₃ is most marked when orthopyroxene is adjacent to cordierite or plagioclase. The cores of the orthopyroxene grains have a high Al₂O₃ ranging from 6.5-8.7wt% level which corresponds to X_{A1.M1} contents of 0.14-0.20. Because the core of a grain in the thin-section may not represent the true core of the grain (sectioning effect), only the highest Al₂O₃ value per sample is considered. The lower limit of orthopyroxene cores in all samples is then 7.12wt%. In one sample, LJ2 40.3, a large variation in Al₂O₃ content in the cores was found. The sample shows coarse, cm-sized opx in the leucosome parts and mm-sized opx in the melanosome parts. The highest Al₂O₃ content is found in the core of a 6 mm large grain located in the leucosome, 8.7wt% Al₂O₃ (Appendix A.IV). Charge balance calculations based on four cations and six oxygens yield a ferric iron content of 0.00 to 0.14 p.f.u., with Fe³⁺/ Fe^{total} ranging from 0.00-0.25.

The orthopyroxene in sample VG80 contained 10.0wt% Al_2O_3 (X_{Mg^*} = 0.71). However, this sample is located in the Fallawatra occurrence and the opx composition falls within the compositional range determined for this area, with Al_2O_3 ranging from 8.0 to 10.3wt% accompanied by X_{Mg^*} of more than 0.69 (blue circle in Fig. 7.4; de Groot, 2008). Also the orthopyroxene of a mesoperthite granulite (FN45A) was analysed. It is not associated with an Al-rich phase. The orthopyroxene has significantly lower alumina



Figure 7.4 Composition of orthopyroxene cores in wt% Al_2O_3 vs. $XMg^* = Mg / (Fe^{2+} + Mg)$ space. The blue circle represents the compositional range of orthopyroxene from the Fallawatra occurrence (de Groot, 2008).



Figure 7.5 Sapphirine composition in terms of Al cations vs. Si cations per 14 cations in the formula unit. The diagonal line represents the ideal Tschermak substitution between the end-member compositions: 7:9:3 and 2:2:1. Blue diamonds indicate sapphirine analyses of sample LJ2 40.3, with different textural types of sapphirine. The grey symbols plotted on top of the Tschermak substitution line represent values of Al + Fe³⁺.

Mineral	Orthopy	roxene					Sapphirine		
Sample	LJ2 30.0-	opx5	LJ2 40.0A	-opx1	LJ2 40.3-opx1	FN45A-opx4	LJ2 40.3 -spr/sil2	LJ2 40.3 -spr2	LJ2 40.3 -spr4
position	rim	core	rim	core	core	core	sil sympl.	pl	bt + pl + oxides
n	1	2	1	1	9	4	4	6	8
SiO ₂	51.30	50.16	50.60	49.63	49.58	50.56	12.25	12.60	13.29
TiO ₂	0.02	0.06	0.03	0.05	0.05	0.03	0.01	0.01	0.02
AI_2O_3	6.01	7.65	6.79	8.19	8.73	1.59	64.17	61.30	59.45
Cr_2O_3	0.01	0.01	0.00	0.02	0.01	0.00	0.05	0.04	0.06
FeO	16.26	16.52	16.70	16.84	14.96	31.72	7.33	8.47	9.95
MnO	1.00	1.50	2.31	2.16	2.41	0.74	0.80	0.97	1.14
MgO	24.86	23.79	23.50	23.07	24.08	15.39	15.81	15.70	15.40
CaO	0.05	0.05	0.04	0.02	0.07	0.18	0.01	0.01	0.01
Na ₂ O	0.01	0.02	0.02	0.01	0.02	0.01	0.01	0.01	0.01
К2О	-	-	-	-	-	-	0.00	0.00	0.00
Total	99.52	99.76	99.99	99.99	99.90	100.22	100.45	99.12	99.34
Normalised to 4	cations						Normalised to 14 cations		
Si	1.87	1.83	1.85	1.81	1.80	1.93	1.45	1.52	1.61
Ті	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Al(IV)	0.13	0.17	0.15	0.19	0.20	0.07	4.55	4.48	4.39
Al(VI)	0.12	0.15	0.14	0.16	0.17	0.07	4.40	4.22	4.09
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01
Fe ³⁺	0.01	0.02	0.02	0.03	0.04	0.00	0.15	0.26	0.30
Fe ²⁺	0.48	0.49	0.49	0.49	0.42	0.90	0.58	0.59	0.71
Mn	0.03	0.05	0.07	0.07	0.07	0.00	0.08	0.10	0.12
Mg	1.35	1.29	1.28	1.25	1.30	1.01	2.79	2.82	2.78
Са	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
К	-	-	-	-	-	-	0.00	0.00	0.00
XMg	0.74	0.73	0.72	0.72	0.76	0.53	0.794	0.768	0.734
XMg*	0.73	0.72	0.71	0.71	0.74	0.53	0.829	0.826	0.797
Fe ³⁺ /Fe ^{tot}	0.02	0.04	0.03	0.05	0.85	0	0.21	0.31	0.30

Table 7.3 Representative mineral compositions for orthopyroxene, sapphirine, garnet, sillimanite, corundum, magnetite and Ti-hematite.

FeO as total Fe oxides. n – number of analyses; opx – orthopyroxene; spr – sapphirine; sil – sillimanite; bt – biotite; pl – plagioclase; X_{Mg} = Mg/ (Fe^{tot} + Mg); X_{Mg*} = Mg/ (Fe²⁺ + Mg);.

Table	7 2	Constinued
rapie	1.3	Continued

Mineral	Garnet				Cordierite			Sillimanite	Corundum	N	lagnetite	Ti-Hematite
Sample	FN21-grt1		LJ2 30.0-g	rt3	FN27-crd1	FN72A-crd3	LJ2 30.0-crd4	LJ2 40.3-sil3	LJ2 40.3-crn1	L	2 40.3-ox3	LJ2 40.3-ox2
position	rim	core	rim	core								
n	2	3	2	2	2	4	3	7	4		5	4
SiO ₂	39.19	39.44	40.16	40.35	48.88	48.66	48.29	37.05	0.00		0.10	0.00
TiO ₂	0.01	0.02	0.02	0.01	-	-	-	0.01	0.01		0.01	12.49
Al2O ₃	22.05	21.93	22.71	22.70	32.57	32.56	32.70	61.72	98.99		0.28	0.21
Cr2O ₃	0.03	0.01	0.00	0.00	-	-	-	0.02	0.03		0.23	0.12
FeO	29.95	29.46	22.15	21.81	2.71	3.77	2.11	1.01	1.02		92.82	78.62
MnO	1.95	1.94	4.65	4.57	0.17	0.33	0.25	0.01	0.00		0.04	0.09
MgO	7.11	6.87	11.16	11.30	11.19	10.69	11.49	0.00	0.00		0.08	0.20
CaO	1.22	1.82	0.93	0.99	0.00	0.00	0.00	0.00	0.00		-	-
Na ₂ O	0.00	0.01	0.01	0.00	0.03	0.03	0.02	0.00	0.00		-	-
K ₂ O					0.03	0.01	0.00	0.01	0.00		-	-
Total	101.50	101.49	101.78	101.72	95.59	96.04	94.86	99.83	100.07		93.55	91.73
Normalise	d to 8 cation	5			11 cations			3 cations	2 cations	3	cations	2 cations
Si	3.02	3.04	3.00	3.01	5.05	5.03	5.01	1.00	0.00		0.00	0.00
Ti	0.00	0.00	0.00	0.00	-	-	-	0.00	0.00		0.00	0.25
Al	2.00	1.99	2.00	2.00	3.97	3.96	4.00	1.97	1.99		0.01	0.01
Cr	0.00	0.00	0.00	0.00	-	-	-	0.00	0.00		0.01	0.00
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.02	0.01		1.97	1.50
Fe ²⁺	1.93	1.90	1.38	1.36	0.23	0.33	0.18	0.00	0.00		1.00	0.24
Mn	0.13	0.13	0.29	0.29	0.01	0.03	0.02	0.00	0.00		0.00	0.00
Mg	0.82	0.79	1.24	1.26	1.72	1.65	1.78	0.00	0.00		0.00	0.01
Ca	0.10	0.15	0.07	0.08	0.00	0.00	0.00	0.00	0.00		-	-
Na	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.00	0.00		-	-
К	-	-	-	-	0.00	0.00	0.00	0.00	0.00		-	-
X _{Mg}	0.30	0.29	0.47	0.48	0.88	0.83	0.91	-		XMg	0.00	0.00
X _{Mg*}	0.30	0.29	0.47	0.48	-	-	-	-		XMg*	0.00	0.03
Xprp	0.27	0.27	0.41	0.42	-	-	-	-		Fe ₂ O ₃	68.50	75.37
X _{alm}	0.65	0.64	0.46	0.46	-	-	-	-		FeO	31.19	10.80
X _{grs}	0.03	0.05	0.02	0.03	-	-	-	-		Fe ³⁺ /Fe ^{tot}	0.66	0.86
X _{sps}	0.04	0.04	0.10	0.10	-	-	-	-		Xilm	-	0.125

FeO as total Fe oxides. n – number of analyses; grt – garnet; crd – cordierite; sil – sillimanite; crn – corundum; ox – oxide; $X_{Mg}=Mg/(Fe^{tot}+Mg)$; $X_{Mg*=}Mg/(Fe^{2+}+Mg)$; $X_{prp} = Mg/(Fe^{2+}+Mn+Mg+Ca)$; $X_{alm}=Fe^{2+}/(Fe^{2+}+Mn+Mg+Ca)$; $X_{grs}=Ca/(Fe^{2+}+Mn+Mg+Ca)$; $X_{sps}=Mn/(Fe^{2+}+Mn+Mg+Ca)$; $X_{ilm}=Ti/(Ti+Fe^{tot})$.



Figure 7.6 X_{Mg} compositional variation of cordierite per Bakhuis Granulite Belt sample. $X_{Mg} = Mg / (Fe^{tot} + Mg)$

and X_{Mg} (Al₂O₃ = 1.6wt%; X_{Mg*} = 0.53. The low Al level of the opx reflects the rock composition.

Sapphirine - Sapphirine compositions from quartz-bearing BGB samples lie close to the ideal 7(Mg,Fe)O: $9Al_2O_3$: $3SiO_2$ end-member, with values trending towards the 2:2:1 end-member composition (2(Mg,Fe)O: $2Al_2O_3$: $1SiO_2$; Higgins et al., 1979; Fig. 7.5). If Al is plotted against Si, all analysed sapphirine grains plot below the ideal Tschermak's substitution line (Si(Mg,Fe²⁺) = (2Al), indicating the incorporation of Fe³⁺ in the structure. Based on charge balance calculations with 14 cations and 20 oxygens, the ferric iron contents are calculated to be 0.15-0.31 cations p.f.u. and Fe³⁺/Fe^{total} ranges between 0.21-0.31. If (Al + Fe³⁺) is plotted against Si a perfect fit with the ideal line is obtained (grey diamonds Fig. 7.5). Sapphirine is consistently more magnesian than Al-rich orthopyroxene with X_{Mg^*} values of 0.795-0.829. In one sample, LJ2 40.3 (blue diamonds in Fig. 7.5; Table 7.3), significant compositional variation of the sapphirine in Al, Mg, Fe and Si is present. This variation is associated with the textural position of sapphirine. Sapphirine associated with sillimanite presents the highest Al₂O₃ content (59.45wt%) and highest iron content (9.95wt% FeO as FeO^(tot)).

Cordierite - Cordierite has a homogeneous, highly magnesian composition in all analysed samples, with

 X_{Mg} values comprised between 0.83-0.94 (Fig. 7.6). It presents the highest X_{Mg} of all coexisting ferromagnesian phases (Fig. 7.7). Alkalies (Na₂O, K₂O) and CaO make up less than 0.05wt% each. Low total sums of 94.06 - 97.47wt% indicate the presence of H₂O and/or CO₂. Mineral formulae calculated on the basis of 11cations and 18 oxygens indicate Si uniformly above 5.00 p.f.u. and Al consistently below 4.00 p.f.u., similar to the substitution Si⁺ = Al⁺, proposed by Schreyer et al. (1990) and observed for other UHT terranes (e.g., Dharma Rao et al., 2012).

Garnet - Figure 7.8 shows garnet core compositions with a large spread in X_{pyr} (0.27-0.45) and X_{alm} (0.42-0.65). The grossular component varies between 0.02 and 0.06 and X_{sps} ranges from 0.01 to 0.14. The cores are richer in pyrope, slightly richer in Ca, and



Figure 7.7 Ternary Al – Fe²⁺ - Mg diagram with the compositional range of BGB metapelite Fe-Mg phases. The phases exhibit the partitioning sequence: $X_{Mg^*}(crd) > X_{Mg^*}(spr) > X_{Mg^*}(opx) > X_{Mg^*}(grt)$. Crd - cordierite; spr - sapphirine; opx - orthopyroxene; grt - garnet.

depleted in almandine. As discussed in Chapter 6, there are three distinct poikiloblastic garnet types that can be recognised in the BGB a) grt enclosing coarse UHT minerals, such as spr and opx (sample VG80), b) grt with fine inclusions of qz and pl (sample FN21), c) grt with inclusions of fine bt and sil (sample FN35, FN36, LJ2 30.0 and LJ2 40.3). The garnet in sample LJ2 40.3 is transitional between type a and c, showing inclusions of spr, as well. Sample FN 35 shows garnets of type c, but also some garnets with green spinel inclusions, interpreted as type a, and some garnets of type b. Garnet type a is observed in sample VG80, which is located in the Fallawatra occurrence. With a garnet core composition of X_{pyr} = 0.43-0.45 and X_{alm} = 0.46-0.44 it falls at the pyrope-rich side of the compositional range as determined for the Fallawatra occurrence (blue circle in Fig. 7.8; de Groot, 2008). Garnets of type b (sample FN21) yield the lowest pyrope content and X_{Mg} (0.27 and 0.30, respectively). Samples LJ2 30.0 and LJ2 40.3 contain garnets of type c and a-c. The cores of these garnets consist essentially of a pyrope-almandine solid solution (X_{pyr} = 0.36-0.43; X_{alm} = 0.47-0.42). X_{Mg} ranges from 0.43-0.50. The garnets in sample FN35 and FN36 are also type c garnets. They are richer in almandine component (X_{alm} = ~0.57) and poorer in X_{pyr} (~0.37) compared to the LJ2 samples. Pyrope-rich garnet has not been observed.

Oxides – Opaque material is common in the pelitic gneisses and consists dominantly of titanhematite (Tihematite) and magnetite. Tihematite presents ferrian ilmenite exsolution lamellae. Therefore Tihematite was analysed both with a defocused beam and a grid analysis. For both techniques similar compositions were obtained, yielding $X_{ilm} = Ti / (Fe^{tot} + Ti)$ between 0.057 and 0.157. X_{Fe3}^+ varies between 0.82-0.94 and Cr, Al, Mn and Mg are each lower than 0.01 p.f.u. Magnetite in coexistence with Tihematite is nearly pure Fe₃O₄ except for small amounts of Cr₂O₃ (<1.44wt%) and Al₂O₃ (<0.63wt%). Titaniferous magnetite was not observed in this study.

Other minerals - The composition of sillimanite in the BGB samples is not pure Al_2SiO_5 , but shows consistently incorporation of minor amounts of Fe_2O_3 (1.12-1.92wt%; $Fe^{3+}= 0.02-0.05$ p.f.u.). Corundum is not pure Al_2O_3 but also shows minor Fe_2O_3 (0.73-1.10wt%).



Figure 7.8 Composition of garnet cores in a ternary $(X_{grs}+X_{sps}) - X_{alm} - X_{pyr}$ diagram. The blue circle represents the compositional range of garnet cores in the Fallawatra occurrence (de Groot, 2008). Pyr – pyrope; alm – almandine; grs – grossular; sps – spessartine; $X_{pyr} = Mg / (Fe^{2+} + Mn + Mg + Ca)$; $X_{alm} = Fe^{2+} / (Fe^{2+} + Mn + Mg + Ca)$; $X_{grs} = Ca / (Fe^{2+} + Mn + Mg + Ca)$.

7.3 Whole Rock Geochemistry

7.3.1 Major element composition

Major element variation is depicted in Harker diagrams (Fig. 7.9, 7.10 and 7.11). The incorporated charnockite and granulite compositions are from Klaver (2011). Results of XRF analyses are given in Appendix A.IV along with the LOI, ASI index and CIPW normative values. Sample SB21 whole-rock composition is not incorporated in this report as the analysis total is 89.7wt%.

7.3.1.1 Metapelitic rocks

For XRF analysis of the metapelitic rocks an attempt was made to separate the melanosome from the leucosome. For sample RG1509 this separation was not possible due to the small layer thickness. Therefore, RG1509 represents the bulk composition of a sillimanite gneiss, similar to MKS40 which has been analysed in a previous study (Klaver, 2011). The incorporation of the felsic part is clearly reflected in a higher SiO_2 content compared to the other metapelitic samples (Fig. 7.9). For the other metapelitic rocks the aim was to only analyse the melanosome part for modelling. However, complete separation of the felsic domains could not be accomplished. This is shown by the values of calculated CIPW qz and fsp values. Sample VG93 contains the lowest qz and fsp normative proportions and displays the highest ASI index (283). This suggests that VG93 most closely approximates a pure melanosome.

7.3.1.2 Mesoperthite granulite (FN69)

With a SiO₂ content of 74.0wt% the mesoperthite granulite plots at the high silica end of the compositional trends shown by granulites in the Harker diagrams (Fig. 7.10). The mesoperthite granulite can be distinguished from the granulites only by its considerably higher K₂O content, 3.9wt% compared to values of 0.3-1.8wt%, resp. With an Al₂O₃ content of 14.9wt% the mesoperthite granulite falls within the Al₂O₃ range of the granulites, 13.4-17.2wt%. Similar to the most felsic granulites it has a low FeO, MgO, MnO, CaO and TiO₂ content and a high value of Na₂O and BaO. The leucocrate character corresponds with high normative qz, pl and alkali-fsp. In the QAP-diagram the granulites and charnockites display a different compositional trend (Fig. 7.12). The mesoperthite granulite plots within the charnockite trend as it is significantly more alkali-fsp-rich compared to the granulites.

7.3.1.3 Sillimanite-cordierite granodiorite (FN60)

In the Harker diagrams the sil-crd granodiorite does not fall along the charnockite trends (Fig. 7.11). The granodiorite displays major differences with the charnockite trend, with relative enrichment in Al_2O_3 , FeO and MgO content and depletion of the other main oxides. It is striking that the sil-crd granodiorite has almost a similar composition as sillimanite gneiss RG1509 and closely approximates MKS40. The sil-crd granodiorite is enriched in Na₂O content relative to RG1509. In the QAP diagram FN60 plots in the granodiorite field in between the charnockite and granulite trend. The alumina saturation index indicates that the granodiorite is peraluminous (ASI = 1.69; Fig. 7.13). This means that there is insufficient Ca, Na and K available to incorporate all aluminium in feldspar and consequently Al has to be allocated to Al-rich minerals such as sillimanite and cordierite. The charnockites and granulites are in general metaluminous (ASI <1).



Figure 7.9 Whole rock Harker diagrams, showing the relation between all analysed metamorphic rocks. Oxide sum has been normalised to 100%. Included are a sillimanite-cordierite granodiorite (FN60), a mesoperthite granulite (FN69), pelitic gneisses (squares), and granulites (open circles). Granulite compositions were obtained by Klaver (2011). Symbols are given below diagrams.



Figure 7.10 Whole rock Harker diagrams, showing the comparison of the composition of mesoperthite granulite FN69 with that of granulites (Klaver, 2011). Oxide sum has been normalised to 100%. Open circles represent granulite compositions.



Figure 7.11 Whole rock Harker diagrams, showing the comparison of the composition of sillimanite-cordierite granodiorite FN60 with that of charnockites (Klaver, 2011). Oxide sum has been normalised to 100%. Included are the composition of two metapelitic rocks, MKS40 and RG1509. Open diamonds represent charnockite compositions.



Figure 7.12 Normative QAP diagram (e.g. Streckeisen, 1976). Plotted are CIPW normative abundances. Symbols according to legend in Figure 7.9.



Figure 7.13 Aluminium saturation index (ASI) versus silica (SiO₂, wt%). The arrow illustrates that ASI values of metapelitic rocks are high, up to 283, plotting outside the graph. ASI is calculated as molar AI / (Na + K + Ca). Symbols according to legend in Figure 7.9.

7.3.2 FeO titration

The results of Fe(II) titration are presented in Table 7.4, with Fe_2O_3 calculated by difference. The method was applied several times to an individual sample in order to obtain a reliable FeO analysis. However, repeating the titration gave a large spread as more analyses were made (Fig. 7.14). This did not reduce the problem. If only the first four analyses of each sample are considered, the standard deviation is 0.6-17.0%. Taking all ten analyses into account, the spread in FeO is larger, with a standard deviation up to 22.8%. Only the first four analyses seem to be more reliable as they show more coherent values. The additional analyses will be disregarded. The method does not yield such a large spread for geostandards of basaltic composition. Therefore, it is most likely that the variation depends on the sample material. Three main factors may have caused the large spread: residual phases, grain size and inhomogeneity of sample material. Yokoyama & Nakamura (2002) noticed that spinel is resistant to the acids used within their method. After dissolution of the BGB samples residual material was present (Fig. 7.15a). Using the EDS detector on the Scanning Electron Microscope (SEM) the residual phases were identified dominantly as sillimanite (Fig. 7.15b) with some accessory spinel. Electron microprobe analyses of BGB sillimanite yield up to 2wt% FeO and in the EDS spectrum scans some grains displayed a minor peak for

Table 7.4 FeO titration results.	Fe ₂ O ₃ is calculated by	/ difference
----------------------------------	-------------------------------------------------	--------------

		n=4			n=10		
oxide (wt%)	FeO	FeO*	Fe ₂ O ₃	Fe ³⁺ /Fe ^(tot)	FeO*	Fe ₂ O ₃	Fe ³⁺ /Fe ^(tot)
SB21	13.82	4.87 (3)	9.94	0.48	3.88 (89)	11.04	0.56
SB24	16.94	2.20 (3)	16.38	0.77	1.98 (38)	16.62	0.79
VG93	16.00	6.14 (13)	10.96	0.45	5.45 (70)	11.72	0.49
LJ2 30.0	6.44	5.40 (3)	1.15	0.09	4.41 (92)	2.25	0.19
LJ2 40.3	16.58	5.30 (67)	12.53	0.52	4.29 (95)	13.66	0.59
RG1509	6.95	2.55 (2)	4.90	0.46	2.38 (17)	5.08	0.49

Numbers in parentheses indicate one standard deviation (1 σ) in terms of last significant numbers: 4.87(3) should be read as 4.87 ± 0.03 and 6.14(13) as 6.14 ± 0.13. FeO^{*} - XRF determined FeO content.



Figure 7.14 FeO content versus analysis number of repeated analyses. FeO content was determined by Fe(II) titration for metapelitic rocks from the Bakhuis Granulite Belt.

iron. Incomplete and variable dissolution of sillimanite, particularly for larger grains, might result in variation of FeO level. However, all iron in the sillimanite can be assumed to be trivalent. Therefore, incomplete dissolution of sillimanite should not affect the FeO level. Furthermore, no correlation between amount of residual material and FeO level has been found. Also spinel did not decompose completely. This phase is present in small amount in all analysed samples and is present in geostandard JP-1, as well. Geostandard JP-1 yields the highest variation in FeO content among the geostandards, which is most likely related to the presence of a residual phase. With a Helos KR Sympatec laser particle sizer of the VU University the grain size of a ground sample, FN60, was determined to vary from <8 μ m up to 70 μ m, with a median size of 5 μ m. The presence of such coarse grains clearly caused problems for poorly dissolving minerals such as sillimanite and spinel. Furthermore, a large grain size of part of the material may have resulted in an inhomogeneous rock powder. The inhomogeneity of the rock powder, with comparatively large grains and with fine grains of different density, may have contributed to the problem. Incomplete homogenisation of the sample before taking a portion for titration may have played a role, as well.



Figure 7.15 Residual material after Fe(II) titration. **a.** BSE image of residual material, mostly sillimanite, in LJ30. **b.** SEM EDS spectra of residual sillimanite in sample LJ2 30.0.

7. ANALYTICAL RESULTS

7.4 Zircon Geochronology

7.4.1 Introduction

With the aid of LA-ICP-MS, the zircon U-Pb ages of three rock-types have been acquired: a sillimanite gneiss, a mesoperthite granulite, and a sil-crd granodiorite. Data are given in Table 7.5 and 7.6 and the results are displayed in Figure 7.16 – 7.18. U-Pb data of individual zircon data is provided in Appendix A.V. 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 analysis. If the scatter is caused only by analytical error, the MSWD is near unity. In practice, any regression with a MSWD >2.5 is considered an errorchron. Also probability density plots are presented. The advantage of probability density plots of Pb-Pb or U-Pb ages is that they allow to distinguish between zircon populations with different ages. Probability density plots are generated using Isoplot 3.71 (Ludwig, 2008) taking into account the errors on the ratios as determined by Iolite. Also conventional ²⁰⁶Pb/²³⁸U versus ²⁰⁷Pb/²³⁵U concordia diagrams (Wetherill, 1956) are given, with the U-Pb ages calculated using Iolite normalised data and Isoplot 3.71 (Ludwig, 2008). Decay constant errors are incorporated and displayed as ellipsoids in the concordia plot. In this study the individual analyses are scattered around the concordia and both weakly normal discordant and weakly reverse discordant analyses are present. This is commonly seen in LA-ICP-MS analyses of zircon. Normal discordance can be explained by lead-loss or uranium-gain. Reverse discordance means either uranium-loss or lead-gain, both of which are geologically hard to justify, in particular in combination with a partial normal discordance. Therefore, the weak reverse discordance (and probably also the weak normal discordance) are most likely caused by Pb-Pb elemental fractionation during ablation (Mezger & Krogstad, 1997). The lower concordia intercept is then usually rather near to the present time (Wijbrans, pers. comm.). The U-Pb system provides ²⁰⁷Pb/²³⁵U, ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²⁰⁶Pb ages. For LA-ICP-MS zircon analyses ²⁰⁷Pb/²⁰⁶Pb age is suggested to be more reliable as it does not take the uranium component into account, eliminating elemental fractionation effects between U and Pb. It should, however, be kept in mind that if ²⁰⁷Pb/²⁰⁶Pb ages are considered, concordance of the sample is assumed. For discordant samples, the age will be underestimated.

7.4.2 Sillimanite gneiss (MKS40)

For the sillimanite gneiss use of the ²⁰⁷Pb/²⁰⁶Pb age does not appear to be appropriate, both the precision and accuracy of the 207Pb/206Pb data are poor. The same problem was found for standard GJ-1 which was analysed on the same day. The ²⁰⁷Pb/²⁰⁶Pb ages of GJ-1 ranged from 625 Ma to 396 Ma, with an average of 510 Ma, compared to the actual age of 608.5 Ma. The ²⁰⁶Pb/²³⁸U ages ranged from 616-599 Ma and yielded an average age of 610 ± 8 Ma, within error of the published age (Jackson et al., 2004). The ²⁰⁶Pb/²³⁸U and ²⁰⁷Pb/²³⁵U ages of MKS40 are concordant, which indicates that the system remained closed for both Pb and U. Consequently, the ²⁰⁶Pb/²³⁸U age can be assumed to be reliable. For the calculation of the ²⁰⁶Pb/²³⁸U age, the ²³⁸U decay constant proposed by Jaffey et al. (1971) has been used. The fifty-five analyses show ²⁰⁶Pb/²³⁸U ages ranging from 2,185 Ma to 2,024 Ma. The curve in the ²⁰⁶Pb/²³⁸U age probability density diagram displays a kink in one of the slopes (Fig. 7.16a). This suggests two distinct age populations. Based on BSE zircon images the two populations could be distinguished. When plotted in a probability density diagram both groups show a Gaussian distribution (Fig. 7.16b). The youngest population yields a weighted ${}^{206}\text{Pb}/{}^{238}\text{U}$ average age of 2,073 ± 7 Ma (95% confidence, MSWD = 1.5), which is in good agreement with the concordia age of $2,066 \pm 10$ Ma (Fig. 7.16c). For the older population a weighted average age of $2,131 \pm 11$ Ma (95% confidence, MSWD = 2.1) is obtained, and an upper concordia intercept of $2,129 \pm 30$ Ma.



Figure 7.16 U-Pb zircon results for sillimanite gneiss MKS40. Upper graph: Probability density plot of including ages а histogram showing the frequency of distribution. All analyses are included. Middle graph: Probability density plot of ages. The weighted average mean age is indicated by the dotted grey lines. All analyses are divided in two zircon populations indicated in blue and green. Lower graph:. Conventional concordia plot with 2σ error ellipses. Similar colour indications used as in b. Intercepts for the two groups are provided.

Intercepts at

MSWD = 1,4

Intercepts at

MSWD = 2,2

66

206Pb/238U



Figure 7.17 U-Pb and Pb-Pb zircon results for mesoperthite granulite FN69. **Upper graph:** Probability density plot of 207 Pb/ 206 Pb ages including a histogram showing the frequency of distribution. All analyses are included. **Lower graph:** Conventional concordia plot with 2σ error ellipses. The upper and lower intercept with the concordia is provided.

7.4.3 Mesoperthite granulite (FN69)

The ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ages of twenty-two analyses form a rather narrow normal distribution, yielding a spread between 2,069 ± 23 Ma and 2,020 ± 17 Ma (Fig. 7.17a). The weighted mean ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ age is 2,040.5 ± 6.5 Ma (95% confidence, MSWD = 1.4). The concordia intercepts are poorly defined with a deviation (2 σ) of 190Ma for the upper intercept and a MSWD of 6.2. The ${}^{206}\text{Pb}/{}^{238}\text{U}$ age yields a weighted average of 2,022 Ma, with a much better precision of 16 Ma (2 σ). However, an MSWD of 7.9 indicates that the data are also unreliable. Most data points plot slightly above the concordia (Fig. 7.17b), indicating a slight reverse discordance. This means that the ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ age might be underestimated, but weak reverse discordance is less probable (see discussion above).



Figure 7.18 U-Pb and Pb-Pb zircon results for granodiorite FN60. Upper graph: Probability density plot of ²⁰⁷Pb/²⁰⁶Pb ages including a histogram showing the frequency of distribution. All analyses are included. Middle graph: Probability density plot of ²⁰⁷Pb/²⁰⁶Pb ages. The age estimates as determined by Isoplot 3.71 (Ludwig, 2008) are indicated by the dotted grey lines. The green curve represents a characteristic inherited zircon population and the red curve the remaining analyses. Lower graph: Conventional concordia plot with 2σ error ellipses. Similar colour indications used as in b. Intercepts for the different groups are

Intercepts at

MSWD = 6,7

Intercepts at

MSWD = 3,2

result		²⁰⁷ Pb/ ²⁰⁶ Pb			²³⁸ U/ ²⁰⁶ Pb			Concordia		
Sample	n	Age (Ma)	±2σ	MSWD	Age (Ma)	±2σ	MSWD	Age (Ma)	±2σ	MSWD
MKS40	34	2124	15	3.9	2073	7	1.5	2066	10	1.4
	24	2139	20	2.5	2131	11	2.1	2129	30	3.8
FN69	22	2041	6	1.4	2022	16	7.9	1966	190	6.2
FN60	13	2127	12	1.8	2163	34	27	2121	34	3.2

Table 7.5 U-Pb zircon ages for the dated Bakhuis Granulite Belt samples. Ages indicated with a colour are taken as result.

7.4.4 Sillimanite-cordierite granodiorite (FN60)

The ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ zircon ages of forty-five analyses yield a spread between 2,160 ± 28 Ma and 1,946 ± 48 Ma. This is a significant variation in age which, as indicated by a ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ age probability density plot, should not be attributed to one single population (Fig. 7.18a). BSE images of the zircon grains show a

complex growth history. One distinct population stands out, characterised by a core with oscillatory zoning and the presence of inclusions along the border of the core (Fig. 7.19). Thirteen of the forty-five zircon analyses belong to this group. Plotted in a probability density plot they yield a single peak with Gaussian-like distribution (Fig. 7.18b). The weighted mean is $2,127 \pm 12$ Ma (95% confidence, MSWD = 1.8) with values between 2,160 \pm 28Ma and 2,093 \pm 24 Ma. The remaining data show a large spread in ²⁰⁷Pb/²⁰⁶Pb ages (2,099-1,946 Ma), with a bimodal distribution in the probability density plot (Fig. 7.17b). This suggests the presence of two growth events within this range. It was not possible to separate the two populations on BSE images. Therefore, Isoplot was used to provide



Figure 7.19 Back-scattered electron image of oldest zircon population with characteristic oscillatory zoning in sample FN60 from the Bakhuis Granulite Belt.

an estimate. Isoplot provides an option 'Unmix multicomponent data using Gaussian deconvolution' (Sambridge & Compston, 1994). If the number of components is provided, the program gives an estimated age for each component (population). The so-called relative misfit parameter indicates the degree to which additional components reduce the amount of unexplained scatter of the input data,

		²⁰⁷ Pb/ ²⁰⁶ Pb			relative	²³⁸ U/ ²⁰⁶ Pb			relative
Sample	Component	Age (Ma)	±2σ	fraction	misfit	Age (Ma)	±2σ	fraction	misfit
MKS40	1	2092	13	0.51	0.880	2074	6	0.64	0.848
	2	2161	11	0.49		2139	9	0.36	
FN60	1	1988	11	0.40	0.540	2003	9	0.18	0.365
	2	2073	14	0.33		2095	5	0.54	
	3	2131	11	0.26		2190	7	0.28	
FN60*	1	1987	10	0.55	0.770	2026	7	0.43	0.622
	2	2067	11	0.54		2118	6	0.57	

Table 7.6 Estimated zircon ages using Isoplot. Ages indicated with a colour are taken as result.

FN60* - all zircon analyses exclusive inherited component as separated on BSE images.

relative to their assigned errors. The relative misfit of a single component is 1.00. If all zircon data of the granodiorite are incorporated and the amount of components is set to three the ages obtained are 2,131 \pm 11 Ma, 2,073 \pm 14 Ma, and 1,988 \pm 11 Ma, with a relative misfit of 0.540 (Table 7.6). The oldest age agrees well with the age determined for the zircon population distinguished with BSE images. This supports the reliability of the approach. The age of 2,073 Ma corresponds with the metamorphic age established for MKS40 and the 1,988 Ma represents the youngest zircon growth event. If the zircon grains assigned to the oldest group are excluded from the data set and the amount of components is set to two, the misfit is improved from 0.540 to 0.777. The ages for the two components are 2,067 \pm 11 Ma and 1,987 \pm 10 Ma, nearly identical to the ages found with three components. As a check the unmix function has also been applied to the dataset of sample MKS40. The reliability of the function could be tested, as for the sillimanite gneiss a good separation of the two zircon generations was possible. The ages obtained with the unmix function are within error of the established ages (Table 7.6). It can, therefore, be assumed that the two younger ages found for the granodiorite, although being estimates only, are rather reliable.

8. DISCUSSION

8.1 Geochronology

8.1.1 Sillimanite gneiss

Zircon dating of the high-grade metamorphism in the north-eastern and central parts of the BGB yielded ages between 2,072 Ma and 2,055 Ma (Fig. 8.1, 8.2; de Roever et al., 2003). A younger high-temperature event has been reported for the south-western part of the belt (Klaver, 2011). Charnockite magmatism occurred here around 1,980 Ma, 70 Myr after the high-grade metamorphism. Metamorphism of metapelitic rocks in the SW of the BGB, situated near the charnockites, might have taken place during either of the two high-temperature events. Therefore, the metamorphic age of a sillimanite gneiss from the Kabelebo River in the SW part of the BGB was determined. Two distinct zircon populations are observed in the gneiss, yielding ages of 2,131±11 Ma and 2,073±7 Ma (Fig. 8.2). The latter age coincides within error with the age of high-grade metamorphism in the NE and central part of the BGB, at 2,072 – 2,055 Ma (Fig. 8.2). Therefore, it is concluded that high-grade metamorphism in the SW of the belt occurred at the same time as elsewhere in the belt.

The older age of 2,131 Ma can be interpreted as an inherited population. Presence of an inherited component is caused by sampling problems, as the sampled leucosome contained several small melanosome parts which could not be removed. The age found might indicate that the zircons represent detritus from the TTG-Greenstone Belt, which was formed at approximately 2.18 Ga to 2.13 Ga. Evidence of an Archaean inherited component has not been detected. The presence of inherited zircon cores in a metapelitic rock subjected to temperatures of more than 1000°C is remarkable. In the past it



Figure 8.1 Schematic map of the Bakhuis Granulite Belt displaying ages of high-grade metamorphism (age \pm 2 sigma) obtained from granulitic and metapelitic rocks in the NE and centre of the belt (de Roever et al., 2003) and from samples dated in this study, in the SW part. The 2,067 Ma given for sample FN60 (Zandkreek), is the estimated age of an inherited component. Down.- downstream; ups. – upstream.

was commonly assumed that UHT metamorphism would effectively homogenise and reset older zircons. However, Kooijman (2011) showed that resetting of zircon ages by UHT metamorphism is limited mainly to metamict zircons, leaving other zircons intact.

8.1.2 Mesoperthite granulite

The mesoperthite granulite (Mgr) has a zircon age of $2,041 \pm 11$ Ma. The age is almost within error of the age of the high-grade metamorphism, 2,072 - 2,055 Ma and is clearly older than the age of charnockite magmatism (Fig. 8.2). The mesoperthite granulite is, therefore, interpreted as having been formed during the high-grade metamorphism rather than the younger magmatic event. Consequently, feldspars in the Mgr can be used for thermometry to establish the distribution of UHT metamorphism in the BGB.

8.1.3 Sillimanite-cordierite granodiorite

Zircons from a sil-crd granodiorite (Scg) occurrence along the Zandkreek revealed a complex growth history. Geochronological data show a wide range of ages with three distinct growth events. The complexity and the wide range of values have not permitted to establish precise ages for the events, but an age of each population has been estimated.

The two older ages, 2,127 Ma and 2,067 Ma, correspond with the two ages established for the sillimanite gneiss MKS40. The age of 2,127 Ma is consistent with the 2,131 Ma age of inherited zircons in the sillimanite gneiss. Characteristic oscillatory zoning suggests a magmatic origin of the inherited zircons in the Scg. The zircons might have been derived from magmatic rocks in the TTG-Greenstone Belt. The age estimate of 2,067 Ma is assumed to represent the phase of high-grade metamorphism, as it falls within the age range of 2,072 – 2,055 Ma. This population is inherited, as well. The age estimate of the youngest population is 1,987 Ma. This age is contemporaneous with the charnockite magmatism at 1,980 Ma which suggests that the Scg may be interpreted as part of this magmatic event.



Figure 8.2 Geochronological data for zircon obtained for the Bakhuis Granulite Belt, for sample MKS40 a sillimanite (sil) gneiss from the Kabalebo River downstream, for sample FN69 a mesoperthite granulite (Mgr) from the Kabalebo River upstream, and for sillimanite-cordierite granodiorite (Scg) from the Zandkreek. For the sil gneiss $^{206}Pb/^{238}U$ ages of 2,131±11 Ma and 2,073±7 Ma were determined. The Mgr yields a $^{207}Pb/^{206}Pb$ age of 2,041±6. The Scg provides $^{207}Pb/^{206}Pb$ estimated ages of 2,127±12 Ma, 2067±11 Ma, and 1,987±10 Ma. The purple coloured bar represents the age range of 1,985-1,975 Ma determined for charnockite magmatism in the SW part of the belt (Klaver, 2011) and the blue bar the ages, 2,072-2,055 Ma, as obtained for high-grade metamorphism in the northeast and central part of the Bakhuis Granulite Belt (de Roever et al., 2003).
It is rather unexpected to find three zircon growth events in one rock type. The two older growth events are assumed to be inherited components in the magmatic Scg. The presence of a population with the age of high-grade metamorphism suggests that the Scg was formed from high-grade metamorphic rocks.

8.2 Rock Geochemistry

8.2.1 Mesoperthite granulite

Mesoperthite granulite occurs intercalated between the other granulites at rather many locations. Based on geochronological data it can be assumed that the Mgr and other granulite were formed by the same highgrade event. The Mgr and other granulites can, therefore, safely be considered to belong to the same metamorphic suite. The Mgr resembles the other granulites in composition, except for a conspicuous difference in K_2O content. The granulites follow a K-poor trend, whilst the Mgr displays a significantly higher K_2O content. Klaver (2011) proposed three scenarios to explain the alkali-poor composition of the granulite suite:

1) Low alkali nature of the granulites due to an originally low-potassium precursor (<1wt% K_2O at 60wt% SiO_2);

2) Severe depletion in mobile elements such as alkali metals, uranium and thorium due to dehydration under CO_2 -rich conditions;

3) Loss of potassium content due to some melt extraction.

Because too little geochemical data were present, he did not draw a definite conclusion regarding these scenarios. The first scenario, a low-potassium precursor, can be rejected in view of the local presence of K-rich layers within the suite, as observed in this study. This does not preclude potassium variation in the protolith. Also the second scenario, severe depletion in alkalies, is in contradiction with the presence of K-rich layers. The final scenario, melt extraction, appears to be plausible. Anhydrous melting favours the release of potassium into the melt (Ebadi & Johannes, 1991) and as witnessed by the presence of concordant leucosomes, the granulites experienced at least minor melting during metamorphism. The leucocrate character of the intercalation suggests a leucosomal character, i.e., a melt formed during migmatisation. In the QAP-diagram (Fig. 7.12) the Mgr coincides with the trend of the charnockites, which represent granitoid melts. The preliminary conclusion is drawn that partial melting of the granulites locally was more extensive resulting in a K-rich melt that formed Mgr layers. Consequently, the remaining granulites would be restitic and depleted in potassium and define a K-poor trend as result of melt extraction. If the Mgr represents a melt of the granulites it would have been generated during or slightly before the peak metamorphic event at around 2,070 Ma and might have crystallised at a later stage. This might explain the slightly younger age of the Mgr. However, the age is based on one sample only and more data should be collected for an accurate determination.

8.2.2 Sillimanite-cordierite granodiorite

Geochronological data precludes that the sillimanite-cordierite granodiorite (Scg) was generated during the UHT metamorphic event. Any thermometric information derived from this body would therefore not contribute to the key question of this thesis. However, understanding the genesis of the Scg might provide valuable information regarding the geological history of the BGB. Therefore, based on the limited data available, an attempt will be made to put the Scg into a cohesive framework.

First of all, it should be established whether the Scg occurrence is of magmatic or metamorphic origin. The most convincing evidence is provided by the field relationships. The granodiorite is

homogeneous on sample and outcrop scale, and the characteristic compositional banding of the pelitic gneisses and granulites is totally absent. Within the outcrop several mafic xenoliths are incorporated that have sharp borders and no resorption features. The observations point to a magmatic character of the Scg. On thin-section scale, the sample is highly mylonitised which makes it more difficult to establish the origin. However, the presence of large, euhedral plagioclase crystals in a finer matrix is identical to the texture of the charnockites, also magmatic rocks. Furthermore, the Scg formed during the same event at ~1,980 Ma as the charnockites. There are, however, also significant differences between the two rock types. The Scg contains zircons with clearly inherited components, which are not observed in the charnockites. Zircons in the charnockites show striking sector zoning which is lacking in the Scg zircons. Furthermore, the Scg contains sillimanite and cordierite which do occur in the metapelites of the BGB but have not been observed in the charnockites. The presence of Al-rich phases suggests that the Scg has been derived from an Al-rich melt, contrary to the charnockites. Geochemical data indeed show that the Scg is peraluminous compared to a metaluminous character of the charnockites. The Scg does not only display a higher Al content, but plots for all elements outside the compositional trend of the charnockites. The significant difference in chemical composition may be explained by a different composition of the protolith, the Scg has clear characteristics of S-type granites. It is remarkable that the Scg closely approximates the composition of some pelitic gneisses. This strongly suggests that the Scg represents a melt from metapelitic rocks, whereas the charnockites are thought to have been derived from granulites (Klaver, 2011). The Scg melt must have remained isolated somehow from the large bodies of charnockitic melt nearby, to prevent mixing.

8.3 Ternary Feldspar Temperatures in the Bakhuis Granulite Belt

8.3.1 Why ternary feldspar thermometry?

Prior to this study, ultrahigh metamorphic conditions were indicated only for an area in the NE of the BGB (de Roever et al., 2003; de Groot, 2008). A prerequisite for UHT metamorphism is its regional scale (Harley, 2008). However, mineralogical and thermometric data for the remainder of the BGB were missing so that it was not possible to establish whether the metamorphism was local or on a regional scale, the scale of the BGB. As mentioned in the introduction and Chapter 7, several factors in the BGB prohibit a conventional approach to the determination of P-T conditions and make it rather hard to find data that might support the UHT character of the entire BGB. In view of the weight of this issue the main factors involved will be reviewed here again.

Diagnostic mineral assemblages for UHT metamorphism, such as spr + qz and $opx + sil \pm qz$, are limited to Mg-Al-rich rocks (Harley, 1998a, 2004, 2008). Mg-Al-rich metapelitic rocks are common in the BGB. However, sampling is difficult as a result of poor accessibility of most outcrops. The dense rainforest limits the rock exposure and a poor infrastructure makes it hard to reach most areas, especially if only a short time period is available. At second, the pelitic gneisses in the BGB generally contain only relics of the peak metamorphic assemblages. Leucosomes have been partly molten, but are still present between the melanosome and interaction between the melanosome may have taken place after peak metamorphism. Retrograde reactions have strongly affected the original assemblages, narrowing the chance of finding complete diagnostic mineral assemblages. In addition, subsequent phases of folding and a considerably younger phase of mylonitisation have affected the rocks. As a consequence, extensive recrystallisation of the peak metamorphic assemblages has taken place.

Despite extensive retrogressive metamorphism and deformation some samples have preserved peak metamorphic minerals and, in cases, mineral assemblages. Apart from the typical UHT area in the NE, most pelitic gneisses of the BGB contain coarse sillimanite as the common relic of peak metamorphism. In many cases sil is associated with coarse Mg-rich cordierite, both of which are not indicative of UHT conditions. Rocks with diagnostic UHT minerals are relatively rare, which makes it difficult to evaluate

the extent of UHT metamorphism in the BGB. Alumina-rich opx is diagnostic and might be used for thermometry, but has been found only at rather few locations, insufficient to cover the whole BGB. As a consequence other thermometers are required. In this respect ternary feldspars provide a robust alternative. Ternary feldspars are significantly more common in the BGB than opx and are fairly resistant to retrograde resetting, making them useful for recognising UHT metamorphism. The ternary feldspar geothermometer is widely used, is well calibrated, and has demonstrated its reproducibility and accuracy (e.g., Benisek et al., 2004). It is independent of the effect of fO_2 and pressure has an insignificant influence on the temperatures determined (e.g., Fuhrman & Lindsley, 1988). This allows the comparison of samples from different parts of the BGB as hardly any correction is required for the temperature found within the pressure range of 7-12 kbar.

8.3.2 Reliability of the FL model

This study uses the model of Fuhrman & Lindsley (1988) for several reasons. Nearly all other studies of UHT metamorphism use this model for feldspar thermometry (references see chapter 4), providing a good comparison with their results. The model does not fundamentally differ from most other models except for the model of Benisek et al. (2010). Use of the other models will yield consistently higher temperatures than with the FL model. It is preferred to use the more conservative, lower temperatures of the FL model,



Figure 8.3 Comparison of the 900°C isotherm (P = 10 kbar) computed from the calorimetry-based mixing model of Benisek et al. (2010), with isotherms calculated from mixing models that are based on phase-equilibrium experiments. G 84: Ghiorso (1984); GU 86: Green & Usdansky (1986); NB 87: Nekvasil & Burnham (1987); FL 88: Fuhrman & Lindsley (1988); EG 90: Elkins and Grove (1990); HP 03: Holland & Powell (2003); B 04: Benisek et al. (2004); D 08: Dolejs (2008). Included are the re-integrated feldspar composition of feldspars from sample FN45A in the Bakhuis Granulite Belt. *After Benisek et al. (2010).*

rather than exaggerating the extent of UHT metamorphism in the BGB. The model of Benisek et al. (2010) is distinctly different, with very limited An in orthoclase and Or in An-rich plagioclase. Based on this model, re-integrated perthite compositions would yield significantly higher temperatures than mesoperthite. Because of the large difference with the FL model it seems appropriate to test the Benisek et al. (2010) model on BGB feldspars. For BGB samples with mesoperthite and perthite, both feldspars almost lie on the same isotherm or the perthite even yields higher temperatures than the mesoperthite (Fig. 8.3). This appears to be less probable. The same effect was observed by Jiao & Guo (2011), who concluded that the model of Benisek et al. (2010) was, therefore, unsuitable for their study.

8.3.3 Distribution of feldspar temperatures over the BGB

The ternary feldspars occurring throughout the whole BGB have been used to retrieve the temperature of the high-grade metamorphic event at 2,072 - 2,055 Ma. As shown in Figure 8.4, the metapelitic rocks from the BGB yield peak temperatures consistently higher than 900°C. In the (south-) central part of the BGB metapelites are missing and only granulites are present. Mesoperthite granulites intercalated between the granulites are highly suitable for thermometry. Their age shows that they were formed during the same metamorphic event as the metapelitic rocks. Additional temperature information can thus be provided by mesoperthite granulite layers that occur throughout the BGB, although their rarity and difficult recognition in the field are limiting factors. Intermediate granulites show, in cases, antiperthite with a considerable amount of exsolution. Feldspar temperatures derived from mesoperthite granulite and intermediate granulite samples also are consequently above 900°C (Fig. 8.4). If all data is combined,



Figure 8.4 Schematic map of the Bakhuis Granulite Belt displaying ternary feldspar temperatures (°C). For samples from the same location the sample with the highest temperature was selected. The large red circle represents the Fallawatra occurrence with a temperature range based on four samples (de Groot, 2008). The dotted lines show interpreted temperature zones.

metapelitic rocks and granulites from 15 locations spread over a large part of the BGB consistently yield peak metamorphic temperatures of more than 900°C. This implies that essentially the entire BGB, 3000km², witnessed UHT metamorphic conditions. Since the temperatures obtained are based on one-feldspar thermometry, they represent minimum temperatures. However, one-feldspar temperatures have been argued to closely approach peak temperatures (Braun et al., 1995, O'Brien & Rötzler, 2003; Martignole & Wang, 2011).

For some zones of the BGB data are lacking as samples were not available, in particular in the central part (Fig. 8.4). Such empty zones might be filled up by studying more samples of mesoperthite granulite from the GMD. However, this is not expected to provide much additional information.

Figure 8.4 shows a considerable variation in feldspar temperatures, up to 150°C. It is possible that such different temperatures occurred during metamorphism. However, temperatures established for samples from the same location (Vanamkreek) show a large temperature variation, 82°C, as well. On such a small distance temperatures are not expected to vary that much which raises the question whether the variation of 150°C is realistic. As discussed in Chapter 7 antiperthite may yield lower temperatures than mesoperthite, depending on the amount of exsolution present and is, therefore, less useful for thermometry. Antiperthite in a granulite near the centre (sample LA158.7) gives a high temperature, 1012°C, whereas, antiperthite from a granulite at a nearby location (sample LE34.1) yields a temperature of 918°C. The latter sample had a rather low amount of exsolution. Mesoperthite, on the other hand, is regarded to provide reliable temperatures. If only mesoperthite temperatures are considered, part of the samples, SA714, JJ337 and KG984, record significantly lower temperature, 901°C, 926°C and 919°C, respectively. This implies that significant temperature differences did occur during metamorphism. Figure 8.4 shows two zones recording temperatures at or above 1000°C, and even one, nearly continuous, larger zone with temperatures of 970°C or more.

8.4 High Oxidation State during UHT Metamorphism

Ultrahigh-temperature metamorphism in the NE metapelite area occurred under oxidising conditions (de Roever et al., 2003), as deduced from the common occurrence of opaque minerals such as magnetite and Fe-Ti oxides (unidentified; assumed to be ilmenite). In this study the opaque minerals were analysed by EPMA for one metapelite sample from the Fallawatra occurrence and four samples from the SW, centre and NE part of the belt. Coarse magnetite and Ti-hematite were identified, e.g., between (coarse) orthopyroxene and sillimanite. The presence of magnetite in coexistence with Ti-hematite indicates a high oxidation state (e.g., Spears, 1981). As shown in Figure 8.5, the oxygen fugacity of the assemblage is situated between the upper stability of ilmenite and the hematite-magnetite (HM) buffer. Based on the temperature range obtained from feldspar thermometry, the BGB metapelites analysed most likely witnessed an oxygen fugacity between approximately 10^{-11} to 10^{-6} MPa. Oxidising conditions during UHT metamorphism are also indicated by the incorporation of Fe³⁺ in opx, spr, sil and crn. Sillimanite and corundum contain 1-2wt% and ~1wt% Fe₂O₃, respectively, which is typical for sil and crn formed at markedly oxidising conditions (e.g., Korhonen & Stout, 2004).The incorporation of Fe³⁺ in Al-rich opx is 0.01 - 0.139 p.f.u and in sapphirine 0.15 - 0.380 p.f.u. The high oxidation state is also reflected in the bulk composition of metapelitic rocks, showing X_{Fe}₃₊ of 0.45 to 0.77 for 5 out of 6 samples.

The preferential incorporation of Fe^{3+} may reverse the Mg-Fe distribution between minerals, changing the stable assemblages that can be formed (Hensen, 1986; Powell & Sandiford, 1988). A high oxygen fugacity would lead to a restricted occurrence, or even absence, of Fe-rich silicates and production of Mg-rich silicates instead (Spears, 1981). At high oxidising conditions (partly oxidised) iron partitions into the oxide phases, enriching the silicates in Mg. Garnet is expected to be richer in Fe²⁺ than opx and spr and, therefore, would not be able to form or would have a very limited occurrence. This is the most probable explanation for the consistent lack of garnet from UHT assemblages in the BGB pelitic gneisses. Sapphirine-bearing rocks from Wilson Lake, Canada (e.g., Currie & Gittins, 1988; Korhonen &

Stout, 2004), (northern) Eastern Ghats, India (e.g., Sengupta et al., 1991; Dasgupta et al., 1995), and Labwor Hills, Uganda (e.g., Sandiford et al., 1987) were formed at higher fO_2 . Similar to the BGB metapelites these occurrences show Fe-Ti oxide (magnetite, hemoilmenite, hematite) in association with sapphirine, cordierite and orthopyroxene, but almost invariably lack garnet.

According to Harley (2008), orthopyroxene with XFe³⁺ of <0.12, in slightly oxidised rocks, can still be used for Al-in-opx thermometry because of its low ferric iron level. Sapphirine with XFe³⁺ of <0.3 together with quartz would still be characteristic for UHT metamorphism (Harley, 2008). Despite the high oxidation state during UHT metamorphism in the BGB metapelites, the amount of Fe³⁺ incorporated in opx and spr is relatively limited, with on average XFe³⁺ of 0.11 and 0.27, respectively, much less than expected for highly oxidised rocks.



Figure 8.5 Plot of $\log fO_2$ versus temperature, showing the stability field of magnetite in coexistence with Tihematite in metapelitic rocks from the Bakhuis Granulite Belt (blue area). Temperature limits were obtained by feldspar thermometry. Included are the Hematite-Magnetite (HM) buffer, Quartz-Fayalite-Magnetite (QFM) buffer, and the Ilmenite-out and Ti-hematite-in lines. *After Spears (1981).*

8.5 UHT Mineral Assemblage in the Bakhuis Granulite Belt

The metapelite area in the NE of the BGB shows characteristic UHT mineral assemblages in most of the samples (de Roever et al., 2003; de Groot, 2008):

- Opx + sil + qz;
- A high level of of alumina (up to $10 \text{ wt}\% \text{ Al}_2\text{O}_3$) in the orthopyroxene;
- Sapphirine in qz-rich rocks and, in cases, in contact with qz.

Sapphirine occurs in part of the opx-bearing metapelitic rocks and was not found in samples without opx. Most metapelite samples contain the assemblage opx + sil, the remaining metapelite samples are rich in (coarse) sil, without opx. Coarse, alumina-rich opx in the metapelites is the common and widespread mafic silicate in the pelitic gneisses, despite the presence of considerable retrograde metamorphism and deformation. Cordierite has not been found in this area. The assemblages in the metapelite area represent a typical occurrence of UHT metamorphism, with both opx + sil + qz and spr + qz. The characteristic assemblages are restricted to a 50-100 km² area in a large metapelite zone amidst granulite. The northwestern and eastern parts of this zone do not show common and widespread opx, nor any sapphirine (Fig. 8.6, 8.7). However, coarse crd is a rather common constituent of these metapelites and is more common than the relatively rare (coarse) opx (Fig. 8.8). Cordierite originally was much more common, but large part of cordierite has been replaced by characteristic aggregates of fine-grained sil, opx (with rather low alumina), bt and ky, partly with some cordierite remnants. Coarse sil is the common and widespread component of these rocks. Metapelite areas elsewhere in the BGB show the same minerals, with coarse sillimanite as most common and wide-spread melanosome component, followed by coarse crd (despite



Figure 8.6 Schematic map of the Bakhuis Granulite Belt displaying the distribution of sapphirine (spr). crd – cordierite; sympl – symplectite; sil – sillimanite; opx – orthopyroxene; qz – quartz.



Figure 8.7 Schematic map of the Bakhuis Granulite Belt displaying the distribution of orthopyroxene (opx) within metapelitic rocks. sil – sillimanite; crd – cordierite; n.a. – not analysed, but analysed in thin section.



Figure 8.8 Schematic map of the Bakhuis Granulite Belt displaying the distribution of cordierite (crd) within metapelitic rocks. Open symbol stands for several samples from locations in that area. $X_{Mg} = Mg/(Mg + Fe^{(tot)})$; n.a. – not analysed.

extensive replacement). Alumina-rich opx is relatively rare, it is coarse-grained and associated with coarse crd + sil. Primary spr in qz-rich rocks has not been found, the only exception being the drill-core LJ2 from the SW part of the belt. The core shows abundant aluminous opx associated with crd and some sil and contains one layer rich in spr + sil with much qz and pl but without opx.

There is a clear spatial variation of UHT mineral assemblages in metapelites across the BGB, with on the one hand the presence of much crd and very rare spr and on the other hand the common presence of spr in quartz-bearing rocks, locally in contact with quartz. Furthermore, Al-rich orthopyroxene is abundant and widespread in the Fallawatra occurrence but relatively rare outside this area.

In summary, metapelites outside the typical UHT Fallawatra occurrence show common cordierite and sillimanite, locally associated with Al-rich orthopyroxene. Feldspar thermometry indicates metamorphic temperatures above 900°C for the assemblage, implying UHT metamorphism. The mineral assemblage is characteristic of UHT metamorphism in view of the presence of Al-rich orthopyroxene. However, the orthopyroxene is relatively rare, whilst cordierite is the more common mafic silicate.

8.6 P-T Conditions during UHT Metamorphism

Feldspar thermometry indicated peak metamorphic temperatures of $1000-1050^{\circ}C$ for the typical UHT Fallawatra occurrence in the NE, with Al-rich opx + sil + qz and with spr + qz (de Groot, 2008). Feldspar thermometry in this study showed similar peak metamorphic temperatures for metapelite areas elsewhere in the BGB, such as in the SW. Therefore, the common presence of cordierite and rather rare occurrence of Al-rich opx in the metapelite areas elsewhere does not appear to be the consequence of lower

temperature. Oxygen fugacity was identical for the Fallawatra occurence and metapelitic rocks elsewhere in the BGB. Pressure may have been the dominant factor. At higher pressure, assemblages with crd are replaced by assemblages with opx + sil (phase diagrams in e.g., Harley, 1998a, 2008). Other factors may also have played a role.

In the absence of coeval garnet, geobarometry for the UHT assemblages is hardly possible. The only method feasible, except for thermodynamic modelling, is use of the orthopyroxene composition by itself. This would hold only for reduced rocks (Harley, 2008), not for strongly oxidised rocks such as the BGB metapelites. However, despite the strong oxidation the amount of trivalent iron in orthopyroxene is limited and considerably less than expected. Harley (1998a) argues that if the $Fe^{3+}/Fe^{(tot)}$ content is < 0.1 the influence of Fe^{3+} on phase diagrams is negligible. In a later article, Harley (2008), it is mentioned that low amounts of Fe^{3+} in orthopyroxene in slightly oxidised rocks would typically decrease the Al-in-opx temperature by 20–50°C, if Fe^{3+} / Fe^{total} (opx) is smaller than 0.12. In view of the low amount of incorporated Fe^{3+} in BGB opx, phase diagrams might perhaps provide a reasonable indication of P-T conditions.

The orthopyroxenes associated with sil in the Fallawatra occurrence show a considerable variation in alumina content of 8.0wt% to 10.3wt%, $Al_y = 0.13-0.20$, and $X_{Mg^*} = 0.71-0.76$. Orthopyroxene

compositions with high Al₂O₃ level (~10wt%), from quartzites and qz-veins, were selected for barometry. Outside the Fallawatra occurrence the best opx data are provided by drill-core LJ2 in the SW of the belt. The coarse orthopyroxene from a leucosome at 40.3 m in the drill-core yields the highest Aly level. For both the Fallawatra occurrence and the LJ2 location the peak Al_v values of orthopyroxene would correspond with a pressure of 91/2 kbar and T of 930°C to 1010°C, in the Tateishi et al. (2004) diagram (Fig. 8.9), based on isobars and isotherms from Hensen & Harley (1990). The temperature estimate is lower than the temperature from feldspar thermometry (up to 1030°C), though not considerably. The estimated pressure is higher than the 81/2 kbar assumed by de Roever et al. (2003; based on phase diagrams). If the diagram of Tateishi et al. (2004) may be used for geothermobarometry of the oxidised BGB rocks, the pressure of 91/2 kbar would be more reliable. However, modelling is required to establish the reliability of this pressure.



Figure 8.9 Compositional diagram showing orthopyroxene chemistry in relation to pressure and temperature, including core compositions of opx with high Al_2O_3 (10wt%) from the Fallawatra occurrence and core composition of opx with the highest alumina content (8.7wt%) from drill-core LJ2. Isobars and isotherms are after Hensen & Harley (1990). XAI = AI(VI); X_{Mg*} = Mg/(Mg + Fe²⁺). After Tateishi et al. (2004).

9. CONCLUSIONS AND FUTURE RESEARCH

9.1 Conclusions

Feldspar thermometry of 20 samples from 15 locations throughout the Bakhuis Granulite Belt (BGB) shows peak metamorphic temperatures exceeding 900°C, on a regional scale. Because UHT metamorphism is defined as a type of granulite-facies with a minimum temperature of 900°C (Harley, 1998a), this implies that the entire BGB, 3,000 km², was subjected to UHT metamorphism. In addition, not only metapelites yield such high feldspar temperatures, but also mesoperthite granulites and intermediate granulites with antiperthite. These temperatures are the only evidence for UHT metamorphism in granulites, as they do not contain any mineralogical evidence for UHT metamorphism. As the central part of the belt is free from pelitic gneisses, this was the only way to establish metamorphic temperatures for this part. The feldspar temperatures are not evenly distributed in the belt, but show two large zones at or above 1000°C, up to 1047°C.

Zircon U/Pb dating on a pelitic gneiss from the SW part of the BGB has yielded a metamorphic age of 2,073±7 Ma, coinciding with the late-Transamazonian metamorphic age range, 2,072-2,055 Ma, established for granulites in the NE and central parts of the belt (de Roever et al., 2003). The age of the dated gneiss precludes a relation to the younger high-temperature magmatic event in the SW of the belt which formed charnockites around 1,980 Ma (Klaver, 2011). Consequently, the BGB metamorphic rocks have been formed during a single UHT metamorphic event.

UHT assemblages in BGB metapelitic rocks show a clear regional variation. A characteristic UHT assemblage (Al-rich) opx + sill + qz \pm spr occurs in an area in the NE of the belt and an atypical peak assemblage crd + sil \pm (Al-rich) opx in the remainder of the belt. Although the assemblage crd + sil is not diagnostic of UHT metamorphism, the local occurrence of Al-rich opx (7.1-8.7wt% Al₂O₃), in coexistence with sil, is characteristic. Moreover, feldspar thermometry established that metamorphic temperatures exceeded 900°C, providing a clear indication of UHT metamorphism.

UHT metamorphism occurred under strongly oxidising conditions as shown by the coexistence of magnetite and Ti-hematite and the incorporation of Fe^{3+} in opx, spr, sil and crn. Based on the association of magnetite and Ti-hematite, the oxygen fugacity is estimated to be between 10^{-11} and 10^{-6} MPa. The remarkable absence of coeval garnet in UHT assemblages is assumed to be a direct consequence of the highly oxidising conditions.

Feldspar thermometry for the Fallawatra occurrence, with spr but without crd, yields temperatures of 1010-1030°C. Similar temperatures were established for the SW part where the UHT assemblage includes common crd. The difference in UHT assemblage, with or without crd, is therefore not explained by temperature variation. A slightly higher pressure for the assemblage without crd might be the main factor to explain the difference. Assemblages with opx + sil are the higher-pressure equivalent of assemblages with crd + sil (e.g., Harley, 1998a, 2008). Geobarometry is difficult in the absence of coeval garnet. However, according to Harley (1998a, 2008) opx with low ferric iron, Fe³⁺ <0.12, might still be used for thermobarometry. Despite the high oxidation during opx presents only a low level of Fe³⁺, with Fe³⁺/Fe^{tot} 0.05-0.17 in most samples. Therefore, this study used opx for combined thermometry and barometry. Peak metamorphic pressure for the most Al-rich opx from the Fallawatra occurrence is 9½ kbar, higher than the 8½ kbar suggested by de Roever et al. (2003). The most Al-rich opx from drill-core LJ2 in the SW of the belt yielded a similar pressure of 9½ kbar. This suggests that other factors may have played a role in causing the difference in UHT mineral assemblage. However, the applicability of the geothermobarometer applied to the oxidised BGB rocks is questionable and thermodynamic modelling is required to provide an accurate pressure.

Geochemical data has revealed the existence of an S-type granite in the SW of the BGB. Zircon dating shows that it has formed during the same magmatic event at 1.98 Ga which generated widespread charnockites in the same area (Klaver, 2011). The S-type granite is most likely formed by partial melting

of pelitic gneiss. Subsequently it did not mix with the charnockitic magma nearby. The data provided by this study suggest that the 1.98 Ga magmatic event is more complicated as previously thought.

The potassium-poor signature of the granulites (Klaver, 2011) is in strong contrast with the K-rich composition of a mesoperthite granulite layer found between other granulites in the SW part of the belt. Mesoperthite granulites were also found at several other locations amidst granulites. The analysed mesoperthite granulite is interpreted as a granitic melt generated during or slightly before peak metamorphism. The potassium-poor signature of the granulites is considered to be due to this melt extraction, implying that the granulites represent at least in part restitic rocks. The slightly younger U/Pb zircon age, 2,041±6 Ma, of the mesoperthite granulite might possibly be due to crystallisation upon cooling after peak metamorphism. However, more geochronological data are required for an accurate determination.

9.2 Recommendations for Future Research

 As clearly shown by this study it is of great importance to perform thermodynamic modelling in order to better understand the UHT metamorphism in the BGB. Modelling is especially desired for the obtainment of an accurate pressure of UHT metamorphism which could potentially explain the observed variation in UHT assemblage. In addition, it would be interesting to examine the absence of garnet and unravel the retrograde path.

This study already provides the bulk composition, including Fe_2O_3 and FeO levels, of metapelitic rocks from different parts of the BGB. One should be aware of the fact that a solution model for sapphirine incorporating Fe^{3+} (Kelsey et al., 2004) is not available for Perple_X. ThermoCALC on the other hand does incorporate such a model, but is more time consuming.

- 2) Ternary feldspars examined in this study displayed two interesting phenomenons. One is shown by antiperthitic feldspar. Within a single thin-section the re-integrated compositions of several grains plot on a trend from Or-poor to almost mesoperthitic composition. The processes that could explain this trend are not fully understood. One possibility is Or-poor compositions are formed during the retrograde path and hence yield lower temperatures. Another possibility is that diffusion depleted part of the ternary feldspar grains in potassium level. The other phenomenon is that different ternary feldspar types, such as mesoperthite and perthite, plot on the same isotherm.
- 3) Better constraints on the age of mesoperthite granulites, preferably from different parts of the BGB, are desired in order to establish the exact crystallisation age of the melt. Furthermore, for both the Mgr and the sil-crd granodiorite (Scg) trace element data would provide a better understanding of their origin. In the Scg xenoliths were observed of which some samples were taken. Chemical analysis and age determinations of these xenoliths samples might provide information about the heat source of the high-grade event at ~1.980 Ma.
- 4) This study did not apply the Ti-in-quartz thermometer for reasons mentioned in Chapter 4. However, in few of the abundant rutile needles in many BGB quartz grains, it would be interesting to apply this thermometer to the metamorphic rocks of the BGB for comparison with the ternary feldspar temperatures.
- 5) From an analytical point of view it would be useful to improve the Fe(II) titration method and solve the problem of sample inhomogeneity. As noticed during this study the method incorporates some uncertainties when applied to metapelitic rocks, notably regarding the poor dissolution of large grains of sillimanite and possibly garnet.

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REFERENCES

- Ague, J.J., Eckert, J.O., Xu Chu, Baxter, E.F., Page Chamberlain, C. (2013) Discovery of ultrahightemperature metamorphism in the Acadian orogeny, Connecticut, USA. *Geology*, v. 41, p. 271-274.
- Altenberger, U., Mejia Jimenez, D. M., Günter, C., Sierra Rodriguez, G. I., Scheffler, F., Oberhänsli, R. (2012) The Garzón Massif, Colombia-a new ultrahightemperature metamorphic complex in the Early Neoproterozoic of northern South America. *Miner Petrol*, v. 105, p. 171–185.
- Aranovich, L.Y., Berman, R.G. (1996) Optimized standard state and solid solution properties of minerals II. Comparisons, predictions, and applications. *Contributions to Mineralogy and Petrology, v. 126, p.* 25-37.
- Aranovich, L.Y., Berman, R.G. (1997) A new garnetorthopyroxene thermometer based on reversed Al2O3 solubility in FeO-Al2O3-SiO2 orthopyroxene. *American Mineralogist, v. 82, p. 354-353.*
- Arima, M., Onuma, K. (1977) The Solubility of Alumina in Enstatite and the Phase Equilibria in the Join MgSiO3-MgAl2SiO6 at 10-25 kbar. *Contrib. Mineral. Petrol. v. 61, p. 251-265.*
- **Armstrong, J.T. (1988)** Quantitative analysis of silicate and oxide materials: Comparison of Monte Carlo, ZAP, and $\varphi(\rho z)$) procedures. *E. Newbury, Microbeam Analysis, San Francisco Press, p. 239–246.*
- Avelar V.G. (2002) Geocronologia Pb–Pb em zircão e Sm– Nd em rocha total da porção centro-norte do Estado do Amapá-Brasil: Implicações para a evolução geodinâmica do setor oriental do Escudo das Guianas, Tese de Doutorado, Universidade Federal do Pará, 213 p.
- Avelar, V.G. (2002) Geocronologia Pb-Pb em zircao e Sm-Nd em rocha total da porcao centro-norte do Estado do Amapa – Brasil: implicacoes para a evolucao geodinamica do setor oriental do Escudo das Guianas. *Tese de Doutorado, CPGG-UFPA, Belem, p. 213.*
- Avelar, V.G., Lafon, J.M., Delor, C., Guerrot, C., Lahondère, D. (2003) Archean crustal remnants in the easternmost part of the Guiana Shield: Pb–Pb and Sm– Nd geochronological evidence for Mesoarchean versus Neoarchean signatures. *Géologie de la France 2–3–4*, p. 83–100.
- Baldwin, J. A., Brown, M. & Schmitz, M. D., (2007) First application of titanium-in-zircon thermometry to ultrahightemperature metamorphism. *Geology*, v. 35, p. 295–298.
- Barth, T.E.W. (1951) The Feldspar Geologic Thermometer. Neues Jahrbuch Mineral. Abh., v. 82, p. 143 154.
- Belyanin, G.A., Rajesh, H.M., Sajeev, K & Van Reenen, D.D. (2012) Ultrahigh-temperature metamorphism from an unusual corundum+orthopyroxene intergrowth bearing Al–Mg granulite from the Southern Marginal Zone, Limpopo Complex, South Africa. Contributions to Mineralogy and Petrology, v. 164, p. 457-475.
- Benisek, A., Dachs, E., Kroll, H., (2010) A ternary feldspar mixing model based on calorimetric data: development and application. *Contrib Mineral Petrol*, v. 160, p. 327– 337.
- Benisek, A., Kroll, H., Cemië, L. (2004) New developments in two-feldspar thermometry. *American Mineralogist, v. 89, p. 1496–1504.*
- Berrangé, J.P. (1977) The geology of southern Guyana, South America. Inst. Geol. Sciences, London, Overseas Division, Memoir 4, p. 112.

- Bhagwat, S.B. (2009) Foundation of Geology Volume 1. Global Vision Publishing Ho, ISBN 3-540-64612-4, p. 491-494.
- Bohlen, S. R. (1991) On the formation of granulites. *Journal* of Metamorphic Geology, v. 9, p. 223–229.
- Bosma W., Kroonenberg S.B., Lissa R.V van., Maas K., Roever E.W.F. de (1978) Geological map of Suriname.
- Bosma, W., Kroonenberg, S.B., Mass, K., De Roever, E.W.F. (1983) Igneous and metamorphic complexes of the Guyana Shield in Surinam. *Geol. Mijnbouw*, v. 62, p. 241-254.
- Bosma, W., Kroonenberg, S.B., Van Lissa, R.V., Maas, K., De Roever, E.W.F. (1984) An explanation to the geology of Suriname. *Geol. Mijnb. Dienst Sur.*, v. 27, p. 31-82.
- Brandt S., Schenk V., Raith, M.M., Appel, P., Gerdes, A., Srikantappa, C. (2011) Late Neoproterozoic P-Tevolution of HP-UHT Granulites from the Palni Hills (South India): New Constraints from Phase DiagramModelling, LA-ICP-MS Zircon Dating and insitu EMP Monazite Dating. *Journal of Petrology, v. 52, p. 1813-1856.*
- Braun, I., Raith, M., Ravindra Kumar, G.R. (1996) Dehydration-melting phenomena in leptynitic gneisses and the generation of leucogranites: a case study from the Kerala Khondalite Belt, southern India. J. Petrol., v. 37, p. 1285-1305.
- Brown, M., (2006) Duality of thermal regimes is the distinctive characteristic of plate tectonics since the Neoarchaean. *Geology*, *34*, *961–964*.
- Brown, M., (2007) Metamorphic conditions in orogenic belts: a record of secular change. *International Geology Review*, v. 49, p. 193–234.
- Carrington, D. P., Harley, S. L. (1995) The stability of osumilite in metapelitic granulites. *Journal of Metamorphic* Geology, v. 13, p. 613–625.
- Chang, Z., Vervoort, J.D., McClelland, W.C., Knaack, C. (2006) U-Pb dating of zircon by LA-ICPMS. *Geochemistry Geophysics Geosystems* 7-5
- Collins, W.J. (2002) Hot orogens, tectonic switching, and creation of continental crust. *Geology*, v. 30 (6), p. 535–538.
- Collins, W.J., (2002b) Nature of extensional accretionary orogens. *Tectonics* 21 (4) (Art. No. 1024)
- Currie, K.L., Gittins, J. (1988) Contrasting sapphirine parageneses from Wilson Lake, Labrador and their tectonic implications. *Journal of Metamorphic Geology*, v. 6, p. 603-622.
- Cutts, K., Hand, M., Kelsey, D.E. (2011) Evidence for early Mesoproterozoic (ca. 1590 Ma) ultrahigh-temperature metmorphsim in southern Australia. *Lithos, v. 124, p. 1-16.*
- **Da Rosa-Costa, L., Lafon, J.M., Delor, C. (2006)** Zircon geochronology and Sm-Nd isotopic study: further constraints for the Archean and Paleoproterozoic geodynamical evolution of the southeastern Guiana Shield, north of Amazonian Craton, Brazil. *Gondwana Research*, v. 10, p. 277-300
- Dahlberg, E.H. (1973) Lithostratigraphical correlation of granulite-facies rocks of the Guiana Shield. Secondo Congreso Latino-Americano, Caracas, Venezuela. Also: Geol. Mijnb. Dienst Sur., Med, v. 23, p. 26-33.
- Dall'Agnol R., Costi, H.T., Leite, da S.A.A., De Magalhães, M.S., Teixeira, N.P. (1999) Rapakivi granites from Brazil and adjacent areas. *Precambrian Research*, v. 95, p 9–39.
- Dasgupta, S., Sengupta, P., Ehl, J., Raith, M., Bardhan, S. (1995) Reaction textures in a suite of spinel granulites

from the Eastern Ghats belt, India: Evidence for polymetamorphism, a partial petrogenic grid in the system KFMASH and the role of ZnO and Fe2O3. *Journal of Petrology 36, p. 435-461.*

- De Roever, E.W.F. (1975b) Geology of the central part of the Bakhuis mountains (W Suriname) *Geol. Mijnb. Dienst Sur.*, v. 23, p. 65-101.
- De Roever E.W.F. (1973) Aprovisional lithologic framework of the Falawatra Group. Mem. Secondo Congreso Latino-Americano de Geologia, Caracas, 1973, see Bol. De Geologia Publ.Esp. 7.2, 637-948 (1976) Also: Geol. Mijnb. Dienst Sur., v. 23, p. 65-101.
- De Roever, E.W.F. (1975a, 1977) Provisional lithologic framework of the Falawatra Group, W. Suriname. *Geol. Mijnb. Dienst Sur. Med 23, p.34-44. Also in: Mem. 2ndo Congreso Latinoamericano de Geología, Bol. Geol.* (Caracas) Publ Esp. no. 7, p. 637-648.
- De Roever, E.W.F., Lafon, J.M., Delor, C., Cocherie, A., Rossi, P., Guerrot, C., 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*, v. 2-3-4, p. 175-205.
- De Roever, E.W.F., Lafon, J.M., Delor, C., Guerrot, C. (2010) Orosirian magmatism and metamorphism in Surinam: new geochronological constraints. 45° Congresso Brasileiro de Geologia, Belem (poster)
- Deckart, K., Bertrand, H., Liégeois, J.-P. (2005) Geochemistry and Sr, Nd, Pb isotopic composition of the Central Atlantic Magmatic Province (CAMP) in Guyana and Guinea. *Lithos*, v. 82, p. 289–314.
- Delor, C., De Roever, E.W.F., Lafon, J.M., Lahondère, D., Rossi, P., Cocherie, A., Guerrot, C., 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.
- Delor, C., Lafon, J.M., Lahondère, D., De Roever, E.W.F., Fraga, M.L., Rossi, P. (2001) Paleoproterozoic framework of the Guiana Shield II - continental scale boudinage and ultra-high temperature granulite belt exhumation at 2.07-2.06 Ga. In: VII simpósio de Geologia de Amazônia, Belem, SBG-NO. Resumos Expandidos (CD-ROM)
- Dharma Rao, C.V., Santosh, M., Chmielowski, R.M. (2012) Sapphirine granulites from Panasapattu, Eastern Ghats belt, India: Ultrahigh-temperature metamorphism in a Proterozoic convergent plate margin. *Geoscience frontiers, v. 3, p. 9-13.*
- Diener J.F., Powell, R. (2010) Influence of ferric iron on the stability of mineral assemblages. J. Metamorphic Geol., v. 28, p. 599-613.
- **Dolejs, D. (2008)** Ternary feldspar equilibria and thermodynamic modelling at the granulite-eclogite facies transition. *Annual Report Bayerisches Geoinstitut, Bayreuth*
- Dougan, T.W. (1974) Cordierite gneisses and associated lithologies of the Guri area, northwest Guyana shield, Venezuela. *Contrib. Mineral. Petrol.*, v. 46, p. 317-342.
- 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*, *v. 106 p. 286-295*.
- Elkins, L.T., Grove T.L., (1990) Ternary feldspar experiments and thermodynamic models American *Mineralogist*, v. 75, p. 544-559.
- 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, v. 17 4, p. 515-535.

- Fitton, G. (1997) X-Ray fluorescence spectrometry. In: Gill, R. (ed.), Modern Analytical Geochemistry: An Introduction to Quantitative Chemical Analysis for Earth, Environmental and Material Scientists: Addison Wesley Longman, UK.
- Fitzsimons, I. C. W., Harley, S. L., (1994) The influence of retrograde cation exchange on granulite P–T estimates and a convergence technique for the recovery of peak metamorphic conditions. *Journal of Petrology*, v. 35, p. 543–576.
- Fonarev, V. I., Pilugin, S. M., Savko, K. A. & Novikova, M. A. (2006) Exsolution textures of orthopyroxene and clinopyroxene in high-grade BIF in the Voronezh Crystalline Massif: evidence of ultrahigh-temperature metamorphism. J. of Metamorphic Geology, v. 24, p. 135–151.
- Fonarev, V.I., Graphchikov, A.A., Konilov, A.N. (1991) A consistent system of geothermometers for metamorphic complexes. *International Geology Review*, v. 33 (8), p. 743-783.
- Fraga, L.M., Macambiro, M.J.B., Dall'Agnol, R., 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. J. of South American Earth Sciences, v. 27, p. 247- 257.
- Fraga, L.M., Macambiro, M.J.B., Dall'Agnol, R., 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. J. of South American Earth Sciences, v. 27, p. 247- 257.
- Fraga, L.M., Reis, N.J., Dall'Agnol, R., 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., Reis, N.J., R. Dall'Agnol., Armstrong R. (2008) Cauarane-Coeroene belt - The tectonic southern limit of the preserved Rhyacian crustal domain in the Guyana Shield, northern Amazonian Craton. Abstract, 33th International Geological Congress Oslo, symposium AMS-07, paper 1344505.
- Fraga, L.M.B. (2002) Associação anortosito-mangeritogranito rapakivi (AMG) do Cinturão Guiana Central, Roraima, e suas encaixantes paleoproterozóicas: evolução estrutural, geocronologia e petrologia. Tese de doutorado, CPGG-UFPA, Belém, 351 p.
- Frost, B. R., Chacko, T., (1989) The granulite uncertainty principle: limitations on thermobarometry in granulites. J. of Geology, v. 97, p. 435–450.
- Fu, B., Page, F.Z., Cavosie, A.J., Fournelle, J., Kita, N.T., Lackey, J.S., Wilde, S.A., Valley, J.W. (2008) Ti-inzircon thermometry: applications and limitations. *Contributions to Mineralogy and Petrology*, v. 156, p. 197-215.
- Fuerstenau, M. C., Han, K. N. (2003) Principles of Mineral Processing. Society of Mining, Metallurgy, and Exploration, incl. ISBN 0-87335-167-3.
- Fuhrman, M.L., Lindsley, D.H. (1988) Ternary-feldspar modelling and thermometry. *American Mineralogist v.* 73, p. 201-215.
- Ghiorso M.S. (1984) Activity/composition relations in the ternary feldspars. Contrib Mineral Petrol, v. 87, p. 282-296.
- Ghiorso, M.S. (1984) Activity composition relations in ternary feldspars. Contrib Mineral Petrol 87:282–296

- Gibbs, A.K., Barron, C.N. (1993) The geology of the Guiana Shield. Oxford University Press (New York); Clarendon Press (Oxford) Oxford monographs on geology and geophysics, v. 22, p. 246.
- Gray, A.L. (1985) Analyst 110, 551.
- Green N.L., Usdansky S.I. (1986) Ternary-feldspar mixing relations and thermobarometry. *American Mineralogist*, v. 71, p. 1100-1108.
- Groot, K. de (2008) Geothermo(baro)metry of ultrahightemperature metamorphism in the Bakhuis Mountain, Surinam. MSc-thesis, Vrije Universiteit Amsterdam.
- Guo, J.-H., Peng P., Chen, Y., Jiao, S.-J., Windley, B.F. (2012) UHT sapphirine granulite metamorphism at 1.93-1.92 Ga caused by gabbronorite intrusions: Implications for tectonic evolution of the norther margin of the North China Craton. *Precambrian Research*, v. 222-223, p. 124-142.
- Harley, S. L. (1984) The solubility of Alumina in orthopyroxene coexisting with garnet in FeO-MgO-Al2O3-SiO2 and CaO- FeO-MgO-Al2O3-SiO2. J. of Petrology, v. 25, p. 665–696.
- Harley, S. L. (1989) The origins of granulites: a metamorphic perspective. *Geological Magazine*, v. 126, p. 215–247.
- Harley, S. L., (1998a) On the occurrence and characterisation of ultrahigh-temperature (UHT) crustal metamorphism. In: What Controls Metamorphism and Metamorphic Reactions? (eds Treloar, P.J. & O_Brien, P.) Special Publication Geological Society of London, v. 138, p. 75–101.
- Harley, S. L. (1998b) An appraisal of peak temperatures and thermal histories in ultrahigh-temperature (UHT) crustal metamorphism: the significance of aluminous orthopyroxene. In: Origin and Evolution of Continents (eds Motoyoshi, Y. & Shiraishi, K.), Memoir National Institute Polar Research, Tokyo. Special Issue, 53, 49– 73.
- Harley, S. L. (1998c) Ultrahigh temperature granulite metamorphism (1050_C, 12 kbar) metamorphism and decompression in garnet (Mg70)-orthopyroxene– sillimanite gneisses from the Rauer Group, East Antarctica. J. of Metamorphic Geology, v. 16, p. 541– 562.
- Harley, S. L. (1987) A pyroxene-bearing metaironstone and other pyroxene–granulites from Tonagh Island, Enderby Land, Antarctica: further evidence for very high temperature (>980_C) Archaean regional metamorphism in the Napier Complex. J. of Metamorphic Geology, v. 5, p. 341–356.
- Harley, S. L. (2004) Extending our understanding of ultrahigh temperature crustal metamorphism. J. of Mineralogical and Petrological Sciences, v. 99, p. 140– 158.
- Harley, S. L.(1992) Proterozoic granulite terranes. In: CONDIE, K. (ed.) Proterozoic Crustal Evolution. Elsevier, Amsterdam, p. 301-359.
- Harley, S. L., Hensen, B. J. & Sheraton, J. W., (1990) Two-stage decompression in orthopyroxene-sillimanite granulites from Forefinger Point, Enderby Land, Antarctica: implications for the evolution of the Archaean Napier Complex. J. of Metamorphic Geology, v. 8, p. 591–613.
- Harley, S. L., Motoyoshi, Y., (2000) Al zoning in orthopyroxene in a sapphirine quartzite: evidence for >1120°C UHT metamorphism in the Napier Complex, Antarctica, and implications for the entropy of sapphirine. *Contributions to Mineralogy and Petrology*, v. 138, p.293–307.
- Harley, S.L. (2008) Refining the P-T records of UHT crustal metamorphism. *J. of metamorphic Geology*, v. 26, p. 125-154.

- Harley, S.L., Green, D.H. (1982) Garnet-orthopyroxene barometry for granulites and peridotites. *Nature*, v. 300, p. 697-701.
- Hellstrom, J., Paton, C., Woodhead, J.D., Hergt, J.M. (2008) Iolite: software for spatially resolved LA-(quad and MC) ICPMS analysis. *Mineralogical Association of Canada short course series*, v. 40, p. 343-348.
- Hensen, B. J., (1986) Theoretical phase relations involving garnet and cordierite revisited: the influence of oxygen fugacity on the stability of sapphirine and spinel in the system Mg–Fe–Al– Si–O. Contributions to Mineralogy and Petrology, v. 92, p. 362–367.
- Hensen, B. J., Harley, S. L. (1990) Graphical analysis of P– T–X relations in granulite facies metapelites. In: High Temperature Metamorphism and Crustal Anatexis, Ch. 3 (eds Ashworth, J.R. & Brown, M.), pp. 19–56.Unwin Hyman, London.
- Higgins, J.B., Ribbe, P.H., Herd, R.K., (1979) Sapphirine I. Crystal chemical contributions. *Contributions to Mineralogy and Petrology*, v. 68, p. 349–356.
- Hokada, T. (2001) Feldspar thermometry in ultrahightemperature metamorphic rocks: Evidence of crustal metamorphism attaining _1100_C in the Archean Napier Complex, East Antarctica. *American Mineralogist*, v. 86, p. 932–938.
- Hokada, T., Suzuki, S. (2006) Feldspar in felsic orthogneiss as indicator for UHT crustal processes. J. of Mineralogical and Petrological Sciences, v. 101, p. 260– 264.
- Holland, T., Powell, R., (2003) Activity–composition relations for phases in petrological calculations: an asymmetric multicomponent formulation. *Contrib Mineral Petrol*, v. 145, p. 492–501.
- Hollis, J. & Harley, S. L., (2003) Alumina solubility in orthopyroxene coexisting with sapphirine and quartz. *Contributions to Mineralogy and Petrology, v. 144, p.* 473–483.
- Hurley, P.M., De Almeida, F.F.M., Melcher, G.C., Cordani, U.G., Rand, J.R., Kawashita, K., Vandoros, P., Pinson, W.H., Fairbairn, H.W. (1967) Test of continental drift by comparison of radiometric ages. *Science*, v. 157, p. 495-550.
- IJzerman, R. (1931) Outline of the geology and petrology of Surinam (Dutch Guiana) Martinus Nijhoff, the Hague, the Netherlands, 519 p.
- Jackson, S.E., Pearson, N.J., Griffin, W.L., Belousova, E.A. (2004) The application of laser ablationinductively coupled plasma-mass spectrometry to in situ U-Pb zircon geochronology; *Chemical Geology*, v. 211, p. 47-69.
- Jaffey, F., Glendenin, B., and Essling (1971) Precision Measurement of Half-Lives and Specific Activities of ²³⁵U and ²³⁸U, *Physical Review C*, v. 4 (5)
- Janssens, K., Van Grieken (2004) X-ray based methods of analysis. Comprehensive Analytical Chemistry, chapter 4, p. 129-226
- Jiao S., Guo J., (2011) Application of the two-feldspar geothermometer to ultrahigh-temperature (UHT) rocks in the Khondalite belt, North China craton and its implications. *American Mineralogist, v. 96, p. 250–260.*
- Johnson, R.W. (1998) The Handbook Fluid Dynamics. Springer, ISBN 3-540-64612-4.
- Kelsey, D. E., Clark, C., Hand, M. & Collins, A. S., (2006) Comment on _First report of garnet-corundum rocks from southern India: implications for prograde highpressure (eclogite-facies) metamorphism. *Earth and Planetary Science Letters*, v. 249, p. 529–534.
- Kelsey, D. E., White, R. W., Powell, R. (2003) Orthopyroxene- sillimanite-quartz assemblages: distribution, petrology, quantitative P-T-X constraints

and P-T paths. J. of Metamorphic Geology, v. 21, p. 439–453.

- Kelsey, D. E., White, R. W., Powell, R. (2005) Calculated phase equilibria in K2O–MgO–FeO–Al2O3–SiO2–H2O for silica-undersaturated sapphirine-bearing mineral assemblages. J. of Metamorphic Geology, v. 23, p. 217– 239.
- Kelsey, D. E., White, R. W., Holland, T. J. B., Powell, R. (2004) Calculated phase equilibria in K2O–MgO–FeO– Al2O3– SiO2–H2O for sapphirine–quartz-bearing mineral assemblages. J. of Metamorphic Geology, v. 22, p. 559–578.
- Kelsey, D.E. (2008) On ultrahigh-temperature crustal metamorphism. *Gondwana Research*, v. 13, p. 1-29.
- Kidder S., Avuoac J.-P., Chan Y.-C. (2013) Application of titanium-in-quartz thermobarometry to greenschist facies veins and recrystallized quartzites in the Hs[°]uehshan range, Taiwan. *Solid Earth, v. 4, p. 1–21.*
- Klaver, M. (2011) The relationship between dry granitoid magmatism and UHT-metamorphism Bakhuis granulite belt, western Suriname. *MSc-thesis, Vrije Universiteit Amsterdam.*
- Klein, E.L., Da Rosa-Costa, L.T., Lafon, J.M. (2003) Magmatismo Paleoarqueano (3,32Ga) na região do Rio Cupixi, SE do Amapá, SE do Escudo das Guianas. *In: VII Simp. Geol. Amaz., Manaus. CD ROM.*
- Kooijman, E., Upadhyay, D., Mezger, K., Raith, M.M., Berndt, J., Srikantappa, C. (2011) Response of the U-Pb chronometer and trace elements in zircon to ultrahigh-temperature metamorphism: the Kadavur anorthosite complex, southern India. *Chemical Geology*, v. 290, p. 177–188.
- Korhonen, F.J., Stout, J.H. (2004) Low-variance sapphirine-bearing assemblages from Wilson Lake, Grenville Province of Labrador, in Tollo, R.P., Corriveau, L., McLelland, J., and Bartholomew, M.J., eds., Proterozoic tectonic evolution of the Grenville orogen in North America: Boulder, Colorado, Geological Society of America, v. 197, p. 81–103.
- Kroonenberg, S.B. (1975) Geology of the Sisa Creek area, SW Suriname. *Geol. Mijnb. Dienst Sur.*, v. 23, p. 103-125.
- Kroonenberg, S.B. (1976) Amphibolite facies and granulitefacies metamorphism in the Coeroeni-Lucie area, southwestern Surinam. *PhD Thesis, Univ. Amsterdam; issued in Geol. Mijnb. Dienst Sur., v. 25, p. 101-289.*
- Kroonenberg, S.L., De Roever, E.W.F. (2009) Geological evolution of the Amazonian Craton. in: Amazonia, landscape and species evolution; Wiley-Blackwell.
- La Tour, E.T. (1989) Analysis of rocks using X-ray fluorescence. *The Rigaku J., v. 6.*
- Lafrance, J., Bardoux, M., Voicu, G., Stevenson, R., Machado, N. (1999) Geological and metallogenic environments of gold deposits of the Guiana Shield: a comparative study between St. Élie (French Guiana) and Omai (Guyana) *Exploration and Mining Geology*, v. 8, p. 117–135.
- Lindsley, D.H., Nekvasil, H. (1989) A temary feldspar model for all reasons (abs.) EOS, v. 70, p. 506.
- Lindsley, D.H. (1983) Pyroxene thermometry. Am Mineral., v. 68, p. 477-493.
- Ludwig, K.R. (2008) Isoplot 3.6: a geochronological toolkit for Microsoft Excel. *Berkeley Geochronology Center, Special Publication, v. 4, p.*78.
- Lund, M. D., Piazolo, S. & Harley, S. L. (2006) Ultrahigh temperature deformation microstructures in felsic granulites of the Napier Complex, Antarctica. *Tectonophysics*, v. 427, p. 133–151.
- Martignole J. & Wang Z. (2010) Felspar thermometry of Grenvillian-age UHT migmatites, Mollendo-Camana

Block, Southern Peru. *The Canadian Mineralogist, v. 48, p. 1025-1039.*

- Mezger, K., Krogstad, E.J. (1997) Interpretation of discordant U-Pb zircon ages: an evaluation. J. of Metamorphic Geology, v. 15, p. 127-140.
- Montgomery, C.W., Hurley, P.M. (1978) Total rock U–Pb and Rb–Sr systematics in the Imataca Series, Guyana Shield, Venezuela. *Earth and Planetary Science Letters*, v. 39, p. 281–290.
- Morgunova, A.A., Perchuk, A.L. (2012) Ultrahigh_Pressure Metamorphism in the Archean– Proterozoic Mobile Belt (Gridino Complex, Karelia, Russia) Doklady Earth Sciences, v. 443, p. 412–416.
- Myers, E.R., Heine, V., Dove, M.T. (1998) Thermodynamics of Al/Al avoidance in the ordering of Al/Si tetrahedral framework structures. *Phys. Chem. Minerals*, v. 25, p. 457-464.
- Nekvasil, H., Burnham, C.W. (1987) The calculated individual effects of pressure and water content on phase equilibiria in the granite system. In: Mysen BO (ed) Magmatic processes: physicochemical principles, Geochemical Society. University Park, Pennsylvania
- Newton, R. C., Charlu, T.V., Kleppa, O.J. (1980) Thermochemistry of the high structural state plagioclases. *Geochimica et Cosmochimica v.44. p. 933* to 941.
- Newton, R.C., Perkins, D (1982) Thermodynamicc alibration of geobarometersb asedo n the assemblages garnet-plagioclase orthopyroxen(ecl inopyroxene)quartz. *American Mineralogist*, v. 67, p. 203-222.
- Nogueira, S.A.A., Bettencourt, J.S., Tassinari, C.C.G. (2000) Geochronology of the Salamangone gold deposit host-rocks, Lourenço district, Amapá, Brazil. *Revista Brasileira de Geociências*, v. 30, p. 261–264.
- Norcross, C.E., Davis, D.W., Spooner, E.T.C., Rust, A. (2000) U–Pb and Pb–Pb age constrainsts on Paleoproterozoic magmatism, deformation and gold mineralization in the Omai area, Guyana Shield. *Precambrian Research*, v. 102, p. 69–86.
- **O'Brien, P. J., Rötzler, J. (2003)** High-pressure granulites: formation, recovery of peak conditions and implications for tectonics. *J. of Metamorphic Geology*, v. 21, p. 3–20.
- Oliveira E.C., Lafon J.M., Gioia S.M.L., Pimentel M.M. (2002) Implantação do método Sm-Nd para minerais metamórficos e sua aplicação em rochas da região central do Amapá, Sudeste do Escudo das Guianas. *In: Congresso Brasileiro de Geologia, 41. João Pessoa – PB. SBG. Anais de resumos, p. 502.*
- Paton, C., J. D. Woodhead, J. C. Hellstrom, J. M. Hergt, A. Greig, and R. Maas (2010), Improved laser ablation U-Pb zircon geochronology through robust downhole fractionation correction, *Geochem. Geophys. Geosyst.*, 11, Q0AA06, doi:10.1029/2009GC002618.
- Pattison, D. R. M. & Begin, N. J., (1994) Zoning patterns in orthopyroxene and garnet in granulites: implications for geothermometry. J. of Metamorphic Geology, v. 12, p. 387–410.
- Pattison, D. R. M., Chacko, T., Farquhar, J., McFarlane, C. R. M. (2003) Temperatures of granulite-facies metamorphism: constraints from experimental phase equilibria and thermobarometry corrected for retrograde exchange. J. of Petrology, v. 44, p. 867–900.
- Pilugin, S. M., Fonarev, V. I., Savko, K. A. (2009) Feldspar Thermometry of Ultrahigh Temperature (≥1000°C) Metapelites from the Voronezh Crystalline Massif (Kursk–Besedino Granulite Block) Doklady Earth Sciences, v. 425, p. 201–204.
- Podlesskii, K. K., (2006) Geothermobarometry of Orthopyroxenebearing Aluminous Granulites based on Internally Consistent Thermodynamic Datasets. *Program*

and Abstracts, Granulites and Granulites 2006, Brasilia, p. 67.

- Powell, R., Sandiford, M. (1988) Sapphirine and spinel phase relationships in the system FeO-MgO-Al2O3-SiO2-TiO2-O2 in the presence of quartz and hypersthene. *Contributions to Mineralogy and Petrology*, v. 98, p. 64–71.
- Prakash, D., Arima, M., Mohan, A. (2006) Ultrahightemperature metamorphism in the Palni Hills, South India: insights from feldspar thermometry and phase equilibria. International Geology Review v. 48 (7), p. 619–638.
- Priem et al., 1986/68; Priem, H.N.A., Boelrijk, N.A.I.M., Verschure, R.H., Hebeda, E.H. (1968) Isotopic age determinations on Surinam rocks, 3. Proterozoic and Permo-Triassic basalt magmatism in the Guiana Shield. *Geol. Mijnbouw*, v. 47, p. 17-20.
- Priem, H.N.A., Andriessen, P.A.M., Boelrijk, N.A.I.M., De Boorder, H., Hebeda, E.H., Huguett, A., Th Verdurmen, E.A., Verschure, R.H. (1982) Geochronology of the Precambrian in the Amazonas Region of southeast Colombia (western Guiana Shield) *Geologie en Mijnbouw*, v. 61, p. 229-242.
- Priem, H.N.A., Boelrijk, N.A.I.M., Hebeda, E.H., Verdurmen, E.A.T., Verschure, R.H. (1971) Isotopic ages of the Trans-Amazonian acidic magmatism and the Nickerie Episode in the Precambrian basement of Surinam, South America. *Geol. Soc. Amer. Bull*, v. 82, p. 1667-1680.
- Raase, P. (1998) Feldspar thermomertry: a valuable tool for deciphering the thermal history of granulite-facies rocks, as illustrated with metapelites from Sri Lanka. *The Canadian Mineralogist. v. 36, p. 67-86.*
- Raczek, O., Stoll, B., Hofmann, A.W., 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*, v. 25-1, p. 77-86
- Raimondo, T. Clark, C., Hand, M., Faure, K. (2011) Assessing the geochemical and tectonic impacts of fluidrock interaction in mid-crustal shear zones: a case study from the intracontinental Alice Springs Orogen, central Australia. J. metamorphic Geol., v. 29, p. 821–850.
- Rasband, W.S. (1997) ImageJ, U.S. National Institutes of Health, Bethesda, Maryland, USA. http://imagej.nih.gov/ij/
- Reed, S. J. B., (2005) Electron Microprobe Analysis and Scanning Electron Microscopy in Geology (2nd Ed.), *Cambridge University Press.*
- Ricci, P.S.F., Lafon, J.M., Vasquez, M.L., Carvalho, J.M.A., Klein, E.L., Macambira, E.M.B., (2003) Geology and geochronology of Archean and Paleoproterozoic domains of the southeastern Amapá and northwestern Pará, Brazil—southeastern Guiana Shield. *Géologie de la France*, v. 2–3–4, p. 101–120.
- Roever, de E.W.F. (1975) Geology of the central part of the Bakhuis mountains (W. Surimane) *Geologische Mijnbouw Dienst Suriname, Med., v. 23, p. 65-101.*
- Rollinson H.R. (1993) Using geochemical data: evaluation, presentation, interpretation J. Wiley & Sons.
- **Rollinson, H.R. (1993)** Using geochemical data: evaluation, presentation, interpretation. *Pearson Prentice Hall, 352 p.*
- Rosa-Costa L.T. da, Jean-Michel Lafon, J.-F., Cocherie, A., Delor, C. (2008) Electron microprobe U–Th–Pb monazite dating of the Transamazonian metamorphic overprint on Archean rocks from the Amapa Block, southeastern Guiana Shield, Northern Brazil. J. of South American Earth Sciences, v. 26, p. 445–462.

- Rötzler, J., Romer, R.L. (2001) P–T–t evolution of ultrahigh-temperature granulites from the Saxon Granulite Massif, Germany. Part I: petrology. J. of Petrology, v. 42, p. 1995–2013.
- Sajeev, K., Osanai, Y. (2004) Ultrahigh-temperature Metamorphism (1150_C, 12 kbar) and Multistage Evolution of Mg-, Al-rich Granulites from the Central Highland Complex, Sri Lanka. J. of Petrology, v. 45, p. 1821-1844.
- Sambridge, M.S., Compston, W. (1994) Mixture modelling of multi-component data sets with application to ionprove zircon ages. *Earth Planet. Sci. Lett.*, v. 128, p. 373-390.
- Sandiford M., Powell R. (1991) Some remarks on hightemperature- low pressure metamorphism in convergent orogens. J. of Metamorphic Geology, v. 9, p. 333-340.
- Sandiford, M., Neall, F. B. & Powell, R., (1987) Metamorphic evolution of aluminous granulites from Labwor Hills, Uganda. *Contributions to Mineralogy and Petrology*, v. 95, p. 217–225.
- Sandiford, M., Powell, R. (1990) Some isostatic and thermal consequences of the vertical strain geometry in convergent orogens. *Earth and Planetary Science Letters*, v. 98, p. 154-165.
- Santos, J.O.S., Potter, P.E., Reis, N.J., Hartmann, L.A., Fletcher, I.R., 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. *Geol. Soc. Amer. Bull.*, v. 115, p. 331-348.
- Santos, J.O.S., Van Breemen, O.B., Groves, D.I., Hartmann, L.A., Almeida, M.E., McNaughton, N.J., 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*, v. 131, p. 73-109.
- Santosh, M., Kusky, T., Wang, L. (2011) Supercontinent cycles, extreme metamorphic processes, and changing fluid regimes. *International Geology Review*, v. 53, p. 1403–1423.
- Santosh, M., Omori, S. (2008) CO2 flushing: a plate tectonic perspective. *Gondwana Research*, v. 13-1, p. 86-102.
- Santosh, M., Tsunogae, T., Ohyama, H., Sato, K., Li, L.H., Liu, S.J. (2008) Carbonic metamorphism at ultrahigh-temperatures: Evidence from North China Craton. *Earth and Planetary Science Letters*, 266, p 149-165.
- Schreyer, W., Maresch, W.V., Daniels, P., Wolfsdorff, P. (1990) Potassic cordierites: characteristic minerals for high-temperature, very low-pressure environments. *Contrib. Mineral. Petrol. v. 105, p. 162-172.*
- Schumacher, J.C. (1991) Empirical ferric iron corrections: necessity, assumptions, and effects on selected geothermobarometers. *Mineralogical Magazine*, v. 55, p. 3-18.
- Seck, H.A. (1971a) Koexistierende Alkalifeldspäte und Plagioklase im System NaAlSi3O8 KAlSi3O8-CaAlSi3O8-H2O bei Temperaturen von 650 °C bis 900 °C. Neues Jahrbuch für Mineralogie, Abhandlungen, v. 115, p. 315-345.
- Seck, H.A. (1971b) Der Einflussd es Drucks auf die Zusammensetzung koexistierender Alkalifeldspate und Plagioklase. Contributions to Mineralogy and Petrology, v. 31, p. 67-86.
- Sengupta, P., Dasgupta, S., Batthacharya, P.K., Mukherjee, M. (1990) An orthopyroxene-biotite geothermometer and its application in crustal granulites and mantke derives rocks. J. of Metamorphic Geology, v. 8, p. 191-197.

- Shimizu, H., Tsunogae, T., Santosh, M. (2009) Spinel + quartz assemblage in granulites from the Achankovil Shear Zone, southern India: Implications for ultrahightemperature metamorphism. J. of Asian Earth Sciences, 36, 209-222.
- Smith, J.V. (1974) Feldspar Minerals. Volume 1. Crystal structure and physical properties. Springer-Verlag, Berlin, p. 625.
- Spear, F. S., Wark, D. A. (2009) Cathodoluminescence imaging and titanium thermometry in metamorphic quartz. J. of Metamorphic Geology, v. 27, p. 187-205.
- Spears, F.S. (1981) An experimental study of hornblende stability and compositional variability in amphibolites. *Am. J. Sci., v. 281, p. 697-734.*
- Štípská, P., Powell, R. (2005) Does ternary feldspar constrain the metamorphic conditions of high-grade metaigneous rocks? Evidence from orthopyroxene granulites, Bohemian Massif. J. of Metamorphic Geology, v. 23, p. 627–647.
- Storm, L.C., Spear, F. S. (2009) Application of the titanium-in-quartz thermometer to pelitic migmatites from the Adirondack Highlands, New York. J. metamorphic Geol., v. 27, p. 479–494.
- Svoboda, J. (2004) Magnetic Techniques For The Treatment Of Materials. Springer, ISBN 1-4020-2038-4, Section 2.6.2 Frantz isodynamic separator, p 141-143.
- Sylvester, P. (2001) Laser-Ablation-ICPMS in the Earth Sciences – Principles and Applications. *Mineralogical Association of Canada, ISBN 0-921294-29-8.*
- Tamashiro, I., Santosh, M., Sajeev, K., Morimoto, T., Tsunogae, T. (2004) Multistage orthopyroxene formation in ultrahigh-temperature granulites of Ganguvarpatti, Southern India: implications for complex metamorphic evolution during Gondwana assembly. J. of Mineralogy and Petrology Sciences, v. 99, p. 279-297.
- Tassinari, C.C.G., Munhá, J.M.V., Teixeira, W., Palácios, T., Nutman, A.P., Sousa, C.S., Santos, A.P., Calado, B.O. (2004) The Imataca Complex, NW Amazonian Craton, Venezuela: crustal evolution and integration of geochronological and petrological cooling histories. *Episodes 27, no 1, p. 3–12.*
- Tateishi, K., Tsunogae, T., Santosh, M., Janardhan, A.S. (2004) First report of sapphirine_quartz assemblage from Southern India: implications for ultrahigh-temperature metamorphism. *Gondwana Research*, v. 7, p. 899-912.
- **Thomas, J.B., Watson, E.B. (2012)** Application of the Ti-inquartz thermobarometer to rutile-free systems. Reply to: a comment on: 'TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in quartz' by Thomas et al. *Contrib Mineral Petrol v. 164*, *p. 369–374*.
- Thomas, J.B., Watson, E.B., Spear, F.S., Shemella, P.T., Nayak, S.K., Lanzirotti, A. (2010) TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in quartz. *Contrib Mineral Petrol. DOI* 10.1007/s00410-010-0505-3
- Thorpe, R.I., Hickman, A.H., Davis, D.W., Mortensen, J.K., Trendall, A.F. (1992) U-Pb zircon geochronology of Archean felsic units in the Marble Bar region, Pilbara Craton, West Australia; *Precambrium Research, Elsevier Sience Publishers, v. 56, p. 169-189.*
- Tsunogae, T., Santosh, M., Onsanai, Y., Owada, M., Toyoshima, T., Hokada, T. (2002) Very high-density carbonic fluid inclusions in sapphirine-bearing granulites from Tonagh Island in the Archean Napier Complex, East Antarctica; implications for CO2 infiltration during ultrahigh-temperature (T>1000 °C) metamorphism. Contributions to Mineralogy and Petrology, v. 143, p. 279-299.

- Wark, D.A., Watson, E.B. (2004) Launching the TitaniQ: a titanium-in-quartz thermometer. Geochimica et Cosmochimica Acta, v. 68 (Goldschmidt Conference Abstracts), A543.
- Wark, D.A., Watson, E.B. (2006) TitaniQ: a titanium-inquartz geothermometer. Contributions to Mineralogy and Petrology, v. 152, 743-754.
- Waters, D. J., (1991) Hercynite-quartz granulites: phase relations, and implications for crustal processes. *European J. of Mineralogy, v. 3, p. 367–386.*
- Watson, E. B., Wark, D. A. and Thomas, J. B., (2006) Crystallization thermometers for zircon and rutile. *Contributions to Mineralogy and Petrology, v. 151, p.* 413–433.
- Wells, P.R.A. (1980) Thermal models for the magmatic accretion and subsequent metamorphism of continental crust. *Earth and Planetary Science Letters*, v.46, p. 253-265.
- Wen, S., 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. Trans. Amer. Geophys. Union, v. 37, p. 320-326.
- Whipple, E.R. (1974) A study of Wilson's determination of ferrous iron in silicates. *Chemical Geology, v. 14, p. 223-238.*
- White, R. W., Powell, R. and Holland, T. J. B. (2001) Calculation of partial melting equilibria in the system Na2O-CaO-K2O- FeO-MgO-Al2O3-SiO2-H2O (NCKFMASH) J. of Metamorphic Geology, v. 19, p. 139-153.
- Whitney, D.L., Evans, B.W. (2010) Abbreviations for names of rock-forming minerals. *American Mineralogist*, v. 95, p. 185-187
- 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., Zheng, Y.F. (2004) Further characterisation of the 91500 Zircon crystal. Geostandards and Geoanalytical Research, v. 28-1, p. 9-39.
- Wilson, A. D. (1955) Determination of ferrous iron in rocks and minerals. Bull. *Geol. Surv. G. B. 9, p. 56–58.*
- Wilson, C.J.N., Seward, T.M., Allan, A.S.R., Charlier, B.L.A., Bello, L. (2012) A comment on: 'TitaniQ under pressure: the effect of pressure and temperature on the solubility of Ti in quartz', by Jay B. Thomas, E. Bruce Watson, Frank S. Spear, Philip T. Shemella, Saroj K. Nayak and Antonio Lanzirotti. *Contrib Mineral Petrol*, v. 164, p. 359–368.
- Winter, J.D. (2001) An introduction to igneous and metamorphic petrology. *Prentice Hall*, 697 p.
- Yokoyama, T., Nakamura, E. (2002) Precise determination of ferrous iron in silicate rocks. *Geochimica et Cosmochimica Acta*, v. 66, p. 1085–1093.
- Yuan, H., Gao, S., Liu, X., Li, H., Günther, D., 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*, v. 28-3, p. 353-370.
- Zhai, M.G., and Santosh, M. (2011) The early Precambrian odyssey of the North China Craton: A synoptic overview. Gondwana Research, v. 20, p. 6-25.