Near-Infrared Spectroscopy on Hydrothermal and Low Grade Metamorphic Chlorites from the East Pilbara Granite Greenstone Belts, Pilbara Craton, Western Australia

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#### Abstract

A variety of datasets containing measurements on bulk rock and chlorite composition, and from near-infrared reflection spectroscopy have been studied to test if the composition of chlorite varies with the hydrothermal or metamorphic grade of rocks from the greenstone belts in the Pilbara Craton, Western Australia. The data is derived from samples collected by Brauhart et al. (1998) and Smithies (2007) who collected respectively altered, and non-altered rocks. In addition to the obtained datasets from other authors, this study prepared a selection of non-altered rocks for a microprobe study to measure the chlorite composition.

An estimation of mineral composition based on spectroscopy and microscopy are compared and evaluated with previous work on the samples. The assessment of mineral composition of rocks based on spectroscopy is done by using typical absorption features of the minerals, where the depth of these features was used to estimate its dominance in the rock. This study concluded that both white mica and chlorite are dominant in the reflection spectra of altered and non-altered samples, amphibole is only abundant in the mafic non-altered rocks. This mineral assemblage varies per rock type for non-altered rocks and alteration facies for altered rocks, which coincides with work from other authors on the same samples. Based on the measurements from the microprobe it is concluded that all measured chlorites are tri-octahedral with a dominance in iron and magnesium in the octahedral sheet. The magnesium number of chlorite is compared with the -OH, FeOH and MgOH absorption wavelengths and depths after a continuum removal. This study shows a general trend of a decrease in absorption wavelength with an increasing magnesium number. The magnesium number of chlorite showed a correlation the magnesium number of the bulk rock composition. For the altered rocks this proved to be useful to indicate the discharge zones in hydrothermal altered area. The metamorphic grade did not influence the magnesium number but was a result of the tholeiitic magma series where mafic rocks have a higher magnesium content than the more felsic rocks.

## 1 Introduction

For this research we will focus on the reflection spectrum of chlorites from different rocks formed in different conditions. King and Clark (1989) and Clark et al. (1990) noticed variations in -OH, Fe-OH and Mg-OH absorption features near respectively 1400nm, 2250nm, and 2350nm with the changing magnesium and iron contents in chlorites.

Spectroscopy in the visible to NIR spectrum is a conventional method for studying mineralogy and mineral assemblage of rocks (Clark et al., 1990; King and Clark, 1989). Especially minerals with a brucite-like layer are of special interest because earlier studies revealed that absorption wavelength of hydroxyl absorption feature depends on the cation which has a bonding with hydroxyl (Doublier et al., 2012; Clark et al., 1990). Studies on the characteristics of hydroxyl absorption features on the same samples as used for this study were conducted by Abweny (2012); van Ruitenbeek et al. (2005, 2006) and Huston et al. (1999).

This study focuses on chlorite minerals since it is a common geothermometer where substitution reactions in the mineral can be related to temperatures it was exposed to during formation (Cathelineau, 1988; De Caritat et al., 1993). Because chlorite is a common mineral in hydrothermal systems and in low-grade metamorphic rocks (e.g. greenschist facies) this property of being a geothermometer might be used to estimate the degree of alteration or metamorphic grade. Doublier et al. (2012) correlated the depths of the characteristic absorption features of chlorite with metamorphism in the diagenetic till epithermal zone in rocks different rock types. Also Abweny (2012) concluded that the absorption features could be used to define the metamorphic grade of rocks near the boundary of greenschist and amphibolite facies.

Although several studies have been done about the variation in composition of chlorites due to differences in hydrothermal and/or metamorphic grade (Abweny, 2012; Doublier et al., 2012; Shikazono and Kawahata, 1987; Zane et al., 1998; Zhong et al., 1985), it has never been studied if there is any systematic compositional difference between the chlorites formed by dominantly hydrothermal or metamorphic processes. Because of its characteristic spectrum in near-infrared (NIR) and its property to variate with the composition it is interesting to study the variation of the spectrum between the chlorites of different origins. All together the following research question is formulated: How does the composition of chlorite vary with the hydrothermal or metamorphic grade and how does this correlate with its near-infrared reflection spectrum?

The Pilbara Craton in Western Australia is for this research of special interest. The Pilbara Craton consists of several greenstone belts which are interlocked between granite suites (figure 1.1). These belts are built-up of different lithologies and are affected by burial metamorphism and some are also altered by hydrothermal processes (Smithies, 2007; Brauhart et al., 1998). Chlorite is one of the abundant minerals in these belts as product of metamorphism till greenschist facies or as alteration product. (Van Kranendonk and Pirajno, 2004).

Samples and datasets used for this research are from (Brauhart et al., 1998), and (Smithies, 2007) who collected respectively hydrothermal altered and low grade metamorphic rocks. Abweny (2012) studied the dataset of Smithies (2007) and variations in its NIR reflection spectrum. van Ruitenbeek et al. (2005) studied the hydrothermal altered rocks from Brauhart et al. (1998) and the reflection spectra of white micas in particular.



Figure 1.1: (a)Geological division of the Pilbara Craton (b) Nomenclature granitic suites and greenstone belts in the East Pilbara Terrane adapted from Hickman (2012)

Estimating the metamorphic or hydrothermal grade from the reflection spectrum of chlorite could be useful in many research fields and for exploration purposes. For example in the mining industry the measurements of reflection spectra can be used to estimate the hydrothermal grade and indicate sites of interest for more detailed exploration. Besides terrestrial research it can also be used in planetary research. Several rovers and landers have brought reflection spectrometers to the surface of Mars where hydrothermal alteration is not uncommon (Mustard et al., 2008). Remote sensing for terrestrial or planetary purposes can be tested to map larger area's.

## 2 Literature review

## 2.1 Geological setting

The Pilbara Craton is an area in Western Australia where a combination of rifting and subduction in the Archean epoch has formed several terrains which contains some of the oldest rocks on this planet (Van Kranendonk et al., 2002). This area has formed 3.80-2.83Ga by several periods of volcanic activity which was followed by sedimentary deposit which covers circa 70% of the craton after erosion. These sedimentary are indicated as the Fortescue and Hamersley basins in Figure 1.1. Nowadays circa 60.000km<sup>2</sup> of Archean geology is exposed on the surface. (Hickman, 2012)

The term craton as used in Western Australia is described by Hickman (2012) as "part of the Earths crust that attained stability at a particular time, after which it was little deformed by comparison with adjacent crust". The Pilbara Craton can be divided in multiple terranes, basins, granitic complexes, and greenstone belts/ complexes (Hickman, 2012). In total there are three terranes namely, Kurrana Terrane, East Pilbara Terrane (EPT) and West Pilbara Superterrane which includes Regal, Karratha and Sholl Terrane (Van Kranendonk, 2006) (see figure 1.1).

Most recent geological interpretation of evolution of the area comes from the Pilbara Craton Mapping Project (PCMP) started in 2002 by the Geological Survey Western Australia (GSWA) which is reviewed by Hickman (2012).

The evolution of the Pilbara Craton started circa 3.8Ga, but almost no remnants of an earlier crust (3.8-3.55Ga), marked as proto-EP in Figure 2.1, are exposed these days. Its existence of a crust before the formation of East Pilbara Terrane is supported by geochronolgical and geochemical data (Van Kranendonk et al., 2002). The oldest, exposed area of the Pilbara Craton is the East Pilbara Terrane which is a remnant of a  $100.000 \,\mathrm{km^2}$  and  $15-20 \,\mathrm{km}$  thick volcanic plateau built-up of the Pilbara Supergroup and granitic complexes from the same age, 3.5-3.23Ga (Hickman, 2012). Formation of this plateau was followed by rifting from the EPT around 3.22Ga, which resulted in the formation of the Karratha, and Kurrane Terrane and several basins (Van Kranendonk, 2006). The Soanesville basin and other rift related basins show a succession of epicontinental clastics overlain by layers of deep water volcanics (Hickman, 2012). The Regal Terrane and Mosquito Creek Basin are both interpreted as old oceanic crust which are respectively formed due to rifting of East Pilbara Terrane with both Karratha Terrane as Kurrane Terrane (Van Kranendonk, 2006). The youngest terrane, Sholl Terrane, is composed of intra-oceanic arc volcanic which is deposited above a subduction zone formed by converging of the Regal and Karratha Terrane (Hickman, 2012). This collission continued till 3.07Ga, and during relaxation De Grey superbasin has formed including three granitic supersuite intrusions between 3.02 and 2.94 Ga (Hickman, 2012).



Figure 2.1: Schematic figure of the evolution of the Pilbara Craton and formation of lithologies from the Pilbara Supergroup from 3.8-2.8Ga. (adapted from Hickman (2012))

#### 2.1.1 East Pilbara Terrane

Since all samples collected in the Pilbara Craton are collected in the East Pilbara Terrane, this study focuses on the East Pilbara Terrane (EPT) which is also called the East Pilbara Granite Greenstone Terrane (EPGGT). Inside the Pilbara Craton the East Pilbara Terrane is exposed over 40.000km<sup>2</sup>, but gravitational data indicated that circa 30.000km<sup>2</sup> is overlain by younger sedimentary layers (Hickman, 2012). The exposed part shows large (35-120km in map view) granitic domes with synclinal volcano sedimentary rocks in between (Van Kranendonk et al., 2002). The volcanic plateau which is the basis of the EPT is contains rocks from the Pilbara Supergroup. Volcanic layers from the Pilbara Supergroup can be found in twenty of the eighteen greenstone belts, Wodgina and Cheearra only expose Mesoarchean rocks. The succession of volcanic layers can be related with at least eight volcanic cycles (see figure 2.1). (Van Kranendonk, 2006)

The lithostratigraphy of the Pilbara Supergroup has been revised in 2006 by Kranendonk. This new interpretation divided the Pilbara Supergroup in the Warrawoona, Kelly, and Sulphur Spring Group, only the Warrawoona groups is divided subgroups,



Figure 2.2: Lithology division of the Panorama supergroup according to Hickman (2012) and Van Kranendonk (2006)

namely: Coonterunah, Talga Talga, Coongan, and Salgash. Both the Warrawoona and Kelly group are found in several greenstone belts while the Sulphur Springs group is only observed in two. Because granitic suites from the same ages as the Sulphur Springs group are exposed in a wider area, it is assumed that its due to erosion that these rocks are only found in a small area. The three groups are divided by a hiatus of circa 75my between Warrawoona and Kelly group and 60my between Kelly and Sulphur Spring group (Hickman, 2012). These pauses in volcanic activity were introduced by deformation and metamorphism of the lower group and followed by subaerial erosion and shallow water deposition. These depositions are found as siliclastic rocks, which have formed the Strelley Pool Formation between the Warrawoona and Kelly group, and Leilira Formation below Sulphur Spring Group (Hickman, 2012). In total there are four felsic volcanic formations visible where the formation is correlated with the formation of the four granitic supersuits. (Ultra-)mafic volcanism formed at the base of the volcanic cycle with layers up to 400 meter (see figure 2.2). (Hickman, 2012)

Metamorphism in the EPT is related with contact with the granitic suite where the metamorphic grade decreases from amphibolite facies near the granitic suite to greenschist and prehnite-pumpellyite facies further away from the contact zone. Very low temperature metamorphism is found in the sedimentary basins of De Grey and Fortescue Groups. (Van Kranendonk et al., 2002). A chemistry study by Terabayashi et al. (2003) suggested Archean ocean-floor metamorphism in the North Pole greenstones.

#### 2.1.2 Panorama district

The dataset with rocks collected by Brauhart et al. (1998), comes from a volcanogenic massive-sulfide deposit hydrothermal system in the panorama district in the Soanesville greenstone belt. Strata of volcanic and sedimentary rocks overly the Strelley granite with a general dip to the east. This exposure of rocks provides a cross section through a volcanogenic massive sulfide-bearing volcanic pile and its intrusion. The volcanogenic massive sulfide (VMS) are sited in, or below, a silicified siltstone between the strata of volcanic and sedimentary rocks (Strelley succession) and the overlying rocks of the Gorge Creek Group. This zone is called the Marker Chert. This area is well described by Brauhart et al. (1998, 2000, 2001) who has divided alteration in four major alteration facies namely: background, feldspar-sericite-quartz, sericite-quartz, and chlorite-quartz alteration. In the study of Brauhart et al. (1998) there is made a difference between semiconformable and transgressive alteration zones. The transgressive zones underly known volcanogenic massive sulfide deposits. The formation of these alteration zones is explained by Brauhart et al. (1998) with interaction of rocks with seawater. Convection cells have been formed which are hydrothermally circulated and driven by the granitic suite. Semiconformable alteration zones are probably result of reaction with seawater and high fluid flux. The transgressive alteration zones mark the path of evolved seawater back to the sea floor, which makes it discharge zones and it is considered as the centre of a hydrothermal convection cell.

## 2.2 Chlorite

Chlorite is a group of phyllosilicate minerals, which is etymologically related to the Greek word chloros, which refers to the greenish color of most specimens. Chlorites can be distinguished from micas by the flexibility of the silicate sheets, where micasheets are elastic and chlorite are not due to its perfect mineral cleavage (Deer et al., 2009). The last accepted nomenclature of chlorites (Bayliss, 1975) classifies ten types which differ in cation substitutions.

The main structural formula for chlorite can be written as  $X_{10-12}Y_8$  $O_{20}(OH)_{16}$  with cations for X: Al,  $\overline{\text{Fe}^{2+}}$ ,  $\overline{\text{Fe}^{3+}}$ , Li, Mg, Mn<sup>2+</sup>, Ni, or Zn; and Y: Al, Si, Fe<sup>3+</sup>, or Cr. Structurally chlorite consists of 2:1 sheets (two tetrahedral and one octahedral layer) which is also referred as talc-like layer, and a brucite-like layer which is between the repeating talc-like layers (figure 2.3)(Lauf, 2010). Chlorites can be formed by several processes and different types of host rock. Besides the hydrothermal and diagenetic origin, chlorite is also a common mineral in sedimentary rocks. (Deer et al., 2009)



Figure 2.3: Structural build-up of chlorites. Adapted from Lauf (2010)

#### 2.2.1 Structure

The basics of the chlorite sheet structure is visualized in Figure 2.3, it shows a 2:1 talc-like layer and the octahedral interlayer which is also called the brucite-like layer. The talc-like layer has two tetrahedral layers and one octahedral. Several substitutions in the talc- and brucite-like layers are possible which define the different types of chlorite (see Table 2.1).

The structural formula of both layers can be written as:  $X_6Y_8O_{20}(OH)_4$  for the talc-like layer, and  $X_6(OH)_{12}$  for the brucite-like layer, where X and Y are respectively the octahedral and tetrahedral sites. Both layers are combined in the chemical formula in table 2.1. The tetrahedral site from the talc-like layer are between squared-brackets and octahedral sites in parentheses. The octahedral cations in the brucite-like layer do not have brackets and are placed in the beginning of the formula. In general the talc-like layer has an excess of anions which results in a negative charged layer while the brucite-like is positively charged due to an excess of cations. The amount of cations in the octahedral sites in general 12 but variations are possible. All twelve sites are

occupied when the cations in the octahedral sheets are divalent and every oxygen atom in the mineral is surrounded by three cations, in this case the chlorite is called a trioctahedral chlorite. However, the octahedral sites can also be occupied by trivalent cations which means per three places two are occupied by a trivalent cation and one is vacant to balance the charge of the mineral. So, because every oxygen atom in the chlorite mineral is surrounded by only two cations the mineral is called a di-octahedral chlorite. The classification boundary for di- or tri-octahedral sheet is defined at 10 cations, if the specific sheet has less than 10 cations per  $O_{20}(OH)_{16}$  it is described as di-octahedral. Because octahedral sheets occur in the talc-like layer and the brucite-like layer it is also possible that one layer is tri-octahedral and the other di-octahedral. In general, the first prefix refers to octahedral sheet of the talc-like layer and the second to the brucite-like layer. When the octahedral layer in the talc-like layer is di-octahedral the layer is referred to pyrophyllite instead of talc and when the interlayer is di-octahedral it is referred to gibbsite instead of brucite. (Deer et al., 2009)

## 2.2.2 Chemistry

Classification of clay minerals has always been a problem because of their small particle size and variable degrees of crystal perfection (Bailey,1980). Classification of chlorites was first proposed by Brown and Bailey (1962) and Foster (1962) which was later examined by Bayliss (1975). The nomenclature of chlorite was simplified by the AIPEA (Association Internationale Pour l'Étude des Argiles) Nomenclature Committee during the 1978 Oxford meeting (Deer et al., 2009). It was decided that the end-member must be named according the dominant octahedral cation present. (Bailey, 1980) Chlorite end-members as they were accepted by the I.M.A. Commission on New Minerals and Mineral Names are shown in table 2.1, adapted from Deer et al. (2009).

|                   | Mineral      | Chemical formula   | Key cation         |
|-------------------|--------------|--|--------------------|
| Tri-octahedral    |              |  |                    |
|                   | Clinochlore  | $Mg_6(Mg_4Al_2)[Si_6Al_2O_{20}](OH)16$   | Mg                 |
|                   | Chamosite    | ${\rm Fe}^{2+}{}_{6}({\rm Fe}^{2+}{}_{4}{\rm Al}_{2})[{\rm Si}_{6}{\rm Al}_{2}{\rm O}_{20}]({\rm OH})16$ | $\mathrm{Fe}^{2+}$ |
|                   | Pennantite   | $Mn^{2+}_{6}(Mn^{2+}_{4}Al_{2})[Si_{6}Al_{2}O_{20}](OH)16$   | $Mn^{2+}$          |
|                   | Nimite       | $(Mg,Ni)_6(Ni_4Al_2)[Si_6Al_2O_{20}](OH)16$  | Ni                 |
|                   | Baileychlore | $Zn_6(Zn_4Al_2)[Si_6Al_2O_{20}](OH)16$   | Zn                 |
|                   | Glagolevite  | $Na_2(Mg,Al)_{12}[Si_6Al_2O_{20}](OH)_{16}$  | Na                 |
| Di-octahedral     |              |  |                    |
|                   | Donbassite   | $Al_4(Al_{4.67})[Si_6Al_2O_{20}](OH)_{16}$   | Al                 |
| Di-tri-octahedral |              |  |                    |
|                   | Cookeite     | $Al_4(Li_2Al_4)[Si_6Al_2O_{20}](OH)_{16}$  | Li                 |
|                   | Borocookeite | $Li_{2+6x}Al_{8-2x}[B_2Si_6O_20](OH,F)_{16}$   | B,Li               |
|                   | Sudoite      | $Al_4(Mg_4Al_2)[Si_6Al_2O_{20}](OH)16$   | Mg, Al             |

Table 2.1: Chlorite endmembers as accepted by the I.M.A. Commission on New Minerals and Mineral Names from Deer et al. (2009)

Two apparent minerals are glagolevite and borocookeite. According to Foster (1962) there should not be place for cations like sodium because of its size. Sodium is located between the 2:1 layers and interlayer in the octahedral site. This is only possible when chlorite has the specific IIa structure type, the interlayer sheet is dioctahedral and if substitutions of substantial Al and/or Fe3+ occur in the 2:1 layer. (Krivovichev et al., 2004) Borocookeite is different from the other chlorites due to the different types of cations in the structural formula. As the name suggests it is a variant for cookeite including boron and fluoride. It is the only chlorite where fluoride replaces hydroxyl as bonding material. Both boron as lithium substitute with aluminum where x is a value between 0-0.33 atoms per formula unit. (Zagorsky et al., 2003)

## 2.2.3 Fe-Mg substitution

The most common substitution in chlorites is the Fe-Mg substitution where magnesium and ferrous iron replace each other in the octahedral sites. Other substitutions of divalent cations like Mn, Ni and Zn are not uncommon and give respectively the end members, pennantite, nimite and baileychlore. (Deer et al., 2009)

#### 2.2.4 Aluminum substitutions

Theoretically an equal amount of aluminium should occupy tetrahedral sites as octahedral sites to compensate for charge difference. This theory is described in the Tschermak substitution:  $\mathrm{Si}^{IV}(\mathrm{Mg}, \mathrm{Fe}^{2+})^{VI} = \mathrm{Al}^{IV}\mathrm{Al}^{VI}$ , where IV and VI indicate respectively cations in the tetrahedral and octahedral sheet. Di-/tri-octahedral substitution shows the development of vacancies ( $\Box$  symbol in next formula) in tetrahedral sheet when aluminium substitute for octahedral magnesium and/or ferrous iron:  $\Box^{VI} 2 \text{Al}^{VI} = 3(\text{Mg}, \text{Fe}^{2+})^{VI}$ . As the first sentence suggested the equal amount of aluminium is theoretically and is often not the case, octahedral aluminium is generally higher or lower than tetrahedral and partially replaced by other trivalent cations like ferric iron or chromium. Replacements of divalent cations by trivalent cations occur when the total number of octahedral cations are larger than the total number of tetrahedral cations. Replacement of divalent by trivalent cations occurs in a 2:3 ratio and the general formula of these minerals can be written as  $(\text{R}^{2+}_{6-x-3y}\text{R}^{3+}_{x+2yy})(\text{Si}_{4-xRx3+})O_{10}(\text{OH})_8$ . (Deer et al., 2009)

#### 2.2.5 Occurence and external influences

Several experimental studies have been completed on the behaviour of chlorite to changes in pressure, temperature, fugacity and metamorphic grade Doublier et al. (2012); De Caritat et al. (1993); Zane et al. (1998); Zhong et al. (1985). The relationship with bulk rock composition has also been studied because chlorite is a common mineral in a wide range of rocktypes, such as: low-grade metamorphic rocks (e.g. greenschist facies), in igneous rocks mainly formed by hydrothermal alteration, in iron-rich sedimentary rocks, argillaceous rocks and as weathering product (Deer et al., 2009; De Caritat et al., 1993).

In several studies chlorite has been used as indicator for conditions during their formation such as, metamorphic grade, thermal grade, hydrothermal alteration, and water content. Cathelineau (1988) concluded that a correlation exists between the  $Al^{IV}$  and the temperature in several geothermal fields in the Los Azures system of Mexico. Árkai and Ghabrial (1997) concluded that the increase of  $Al^{IV}$  with increasing metamorphic grade (temperature) is related with a decreasing amount of impurities in the chlorites instead of an increasing isomorphic substitution of Si by Al, this idea was supported by Jiang et al. (1994). Jiang et al. (1994) did not exclude the possibility of a chlorite as a geothermometer but careful analytical work is strongly advised because of the other influences between compositions, thermodynamic variables, and physical conditions of formation of chlorites. Árkai and Ghabrial (1997) concluded that the influence of bulk rock chemistry on chemical composition and crystallinity of chlorite has to be taken into account before tetrahedral aluminium can be used as a geothermometer. In geothermal systems the whole rock composition and chlorite composition is influenced by the interaction with water, so the composition and origin of the water has to be taken into account. Several studies indicated that geothermal systems linked with VMS deposits suggest that the Mg/Mg+Fe ratio increase closer to ore bodies (McLeod et al., 1987). Zhong et al. (1985) studied chlorites from ultramafic bodies from the southern Appalachians in North Carolina and Virgina which were formed by a single protolith, where the bodies differ in the degree of metasomatic alteration. It is concluded that variations Fe/(Fe+Mg) and Al/(Al+Si) are consistent with differing degrees of the same metasomatic process on one single protolith. Zang and Fyfe (1995) studied chlorites in the Igarap Bahia gold deposit in Brazil. They noticed an increase in Fe/(Fe+Mg) ratios from country rock towards the mineralization zone which was attributed to the difference in water/rock ratios and the location in the hydrothermal system. The recharge zones reacted with relatively magnesium-rich fluids while discharge zones reacted with depleted Mg-fluids and more Fe-rich.

## 2.3 Spectral studies

## 2.3.1 Basics

Background information about spectroscopy and its application in mineralogy is well described in Clark (1999): "Spectroscopy is the study of light as a function of wavelength that has been emitted, reflected or scattered from a solid, liquid, or gas". When a photon interacts with a mineral two paths are possible, either it is scattered from the surface or the photon is absorbed. Scattering could mean that it is refracted or reflected. Absorption is a result of multiple processes and based on its wavelength that provides information about the mineralogy. All solids also emit light when its above the absolute minimum temperature of zero Kelvin. (Clark, 1999)

The combination of scattered and emitted photons can be measured by a spectrometer. Where our eyes can only observe the visible part of a spectrum, a spectrometer could have a wider range. For this study most of the spectra have a range from visible  $(0.4 \,\mu\text{m}-0.7 \,\mu\text{m})$  till the short wave infrared  $(1.0 \,\mu\text{m}-2.5 \,\mu\text{m})$ . A spectrometer can measure multiple parts in a spectrum, that's called spectrum sampling. The bandwidth is the width of one measured channel and is an indication for the accuracy of the measurement. Last important feature for a spectrometer is its signal to noise ratio which is an indication of the bandwidth, spectrometer sensitivity and the intensity of light.(Clark, 1999)

Two main processes are involved in the absorption of light namely electronic and vibration. Electronic processes means that a photon interacts with electrons in the atoms which results in light emission. Vibrational processes are molecular processes where atoms interact and have different options of movement reative to each other. This vibration is visible in the infrared when these molecules have a dipole moment. In the NIR wavelength range some combinations of vibrations are visible in the spectrum. The vibrational overtones of  $NH_3$ ,  $H_2O$ ,  $CO_3$ , and OH are visible at particular wavelengths (see Hunt (1977)). Especially the OH vibrational overtones are interesting for this study because the absorption wavelengths changes depending on which cation is bonded (Hunt, 1977).

#### 2.3.2 Minerals

Multiple spectroscopy studies have been done in the Pilbara Craton by Abweny (2012), van Ruitenbeek et al. (2005, 2006), and Huston et al. (1999). From these studies it is known that minerals like amphibole, chlorite, white mica, epidote and carbonate

could be recognized in the reflection spectra in the NIR range. Both van Ruitenbeek et al. (2005) as Huston et al. (1999) used a ratio of the 2200nm feature of white mica and 2250nm of chlorite to study the relative abundance of both minerals in the terrain.

#### Chlorite

The most important mineral for this study is chlorite. Chlorite has three characteristic absorption features in the SWIR range namely an hydroxyl absorption around 1400nm, iron and magnesium hydroxyl bonding absorption near respectively 2250nm and 2350nm (Abweny, 2012). King and Clark (1989) studied the absorption features and if they change with respect to mineral compositions. The absorption feature hydroxyl near 1400nm changed in intensity with the Fe:Mg content in chlorite. Unbound water can be detected near 1900nm in conjunction with 1400nm. Abweny (2012) studied rocks from the Pilbara Craton and correlated the wavelength of FeOH and MgOH absorption features with the magnesium content in the octahedral sheet or chlorite which was related with the metamorphic grade. Doublier et al. (2012) studied the depth of the characteristic absorption features and could relate this with the metamorphic grade. This was done by comparing the depths with ratio's calculated from the X-ray diffraction measurements which can be used to define the diagenetic, anchi- and epizone .

#### White mica

White mica is used as a group name for muscovite, illite, celadonite, and sericite by van Ruitenbeek et al. (2005) and Abweny (2012) because of their similarities in the reflection spectra. These similarities were indicated by Clark et al. (1990) for the minerals: illite, muscovite, and montmorillonite. Characteristic absorption features of AlOH and MgOH are found near 2200 and 2350nm.

#### Epidote

The spectrum of epidote shows many similarities with the spectrum of chlorite (Dalton et al., 2004). Just like chlorite, epidote has FeOH and MgOH absorption features near 2250 and 2350nm. An important secondary absorption feature is found near 1500nm as a result of hydroxyl bond. (Abweny, 2012)

#### Amphibole

Amphibole is characterized in spectra of several rocks from the Pilbara Craton by Abweny (2012). Both hornblende as actinolite can be recognized as amphibole endmembers and have characteristic absorption features near 2350 and 2400nm.

#### Carbonate

In the SWIR range only the absorption feature near 2350nm can be recognized for carbonate minerals like dolomite and calcite (Clark et al., 1990). As described above more minerals have an absorption feature in this range which makes it difficult to characterize in the spectrum. This problem was studied in Dalton et al. (2004) for a chlorite, epidote, carbonate mixture where they were able to classify these minerals in a spectrum after making multiple reference spectra from rocks with known mixtures of chlorite, epidote and carbonate.

## 3 Method

## 3.1 Datasets

For this study there is made use of several datasets from work of different authors Smithies (2007); Brauhart et al. (1998); Abweny (2012); Huston et al. (1999). The locations of the collected samples is shown in Figure 3.1 where the red squares indicate the locations of the samples from Smithies (2007), blue square the sample site of Brauhart et al. (1998). The difference between the samples collected by both authors is that Brauhart et al. (1998) only sampled altered and weathered rocks while Smithies (2007) sampled non-altered, low grade metamorphic (e.g. greenschist facies), volcanic rocks. In this thesis the datasets which contain measurements on the low grade metamorphic volcanic rocks will be termed the metamorphic dataset and datasets with measurements on the altered rocks will be termed the alteration dataset. These datasets were made available by Twente University - Faculty of Geo-information Science and Earth Observation (ITC).



Figure 3.1: Locations of the samples of the alteration dataset from Brauhart et al. (1998) (blue square) and the metamorphic dataset Smithies (2007) (red squares). Map adapted from Hickman (2012)

The alteration dataset contains measurements of the bulk rock composition, chlorite

chemistry, and near infra-red (NIR) reflectance spectra. The spectral data were collected with a portable infra-red mineral analyser (PIMA) in the 1300-2500nm wavelength range by Huston et al. (1999). Bulk rock measurements were collected with X-ray fluorescence on fused disks and pressed pellets by Brauhart et al. (2001). Chemical composition of chlorites and other minerals were measured with an electron microprobe but additional information is not provided by the author.

The metamorphic dataset contains measurements done on rocks collected by Smithies (2007). For his study Smithies (2007) measured the bulk rock composition by using wavelength dispersive X-ray fluorescence on fused disks. Spectral data in the NIR range were collected by Abweny (2012) with an ASD Fieldspec Pro in the 350-2500nm wavelength range. Other than the alteration dataset no microprobe study was available or done on these samples, so measurements will be done in this study (see 3.3 - Electron microprobe).

## 3.2 Spectral data interpretation

The mineral composition of rocks was estimated with the NIR reflection spectra. This is done by making a classification of minerals which are abundant in the spectrum based on absorption depths of the characteristic absorption features (see Figure 3.2). For the spectral interpretation there is made use of software programs like, The Spectral Geologist and HypPy (Bakker and Oosthoek).



Figure 3.2: Reflection spectra of minerals after continuum removal in the visible to short-wave infrared wavelength range. Lines mark some of the characteristic absorption features. Note that the y-axis is not the same for all graphs

The mineral composition and the order of dominance in the spectrum was based on the characteristic features of minerals as shown in figure 3.2. Knowledge for the interpretation of mixed spectra comes from G-MEX booklets and the mineral interpretation of Abweny (2012). Figure 3.2 shows the minerals which were observed in the spectra in both datasets. No difference was made between iron- or magnesium rich chlorites. Actinolite and hornblende are grouped as amphibole. The term white mica refers to spectra of illite, muscovite, or sercite.



Figure 3.3: Some examples of mixed spectra of chlorite with white mica and amphibole after continuum removal. The mineral order in the legend defines which mineral is most dominant in the spectrum and which second and third. Note that all three spectra have their own y-axis with absorption depths.

Figure 3.3 shows some spectra which contain a mixture of minerals in the reflection spectra. Based on the depth of the characteristic absorption features after continuum removal a classification is made in dominance of minerals. For chlorite this was the 2250nm feature, 2400nm for the amphiboles, and 2200nm for white mica. For epidote the 1500nm was used as indicator for its presence in the spectrum (see figure 3.2). This feature could not be used for the mineral classification because it was often only a kink in the graph near 1500nm and not a clear absorption with a minimum to compare with other features.

## 3.3 Electron microprobe

The selection of samples from the metamorphic dataset for the microprobe analysis was based on the dominance of chlorite in the reflection spectra. Table 3.1 was made to see how many times chlorite is classified as most dominant mineral in a greenstone belt or for each rock type. To have a good comparison with the alteration dataset samples were chosen which most likely had the same conditions in geological history. It was assumed that this would be the case for rocks from one greenstone belt and geological formation.

Table 3.1 shows that most samples from Marble Bar had dominant chlorite. The Duffer formation in the Marble Bar provides enough samples for this analysis. Eventually 13 samples where selected: four basalts, four andesites, three dacites and two rhyollites. One of the basaltic rocks and two rhyolite samples did not have chlorite as most dominant mineral in the spectrum but respectively hornblende and sericite. Because Abweny (2012) concluded that all rocks from the amphibolite facies could be distinguished by their lower Mg-OH absorption feature it is tested if this is due to the chlorite composition or the influence of amphibole spectrum. This sample is from the Marble Bar but the Coonterunah subgroup instead of the duffer formation.

|                                | Basalt | Andesite | Dacite | $\operatorname{Rhyolite}$ | Komatitic Basalt | Periodtite/ Komatiite | Komatiite | Peridotite Dyke | Sum |
|--------------------------------|--------|----------|--------|---------------------------|------------------|-----------------------|-----------|-----------------|-----|
| Marble Bar                     | 40     | 9        | 11     | 6                         | 1                | 0                     | 1         | 1               | 69  |
| Warralong                      | 5      | 0        | 0      | 0                         | 3                | 0                     | 1         | 0               | 9   |
| East Strelley                  | 38     | 18       | 5      | 1                         | 0                | 0                     | 4         | 0               | 66  |
| Northwest Kelly                | 9      | 0        | 0      | 0                         | 5                | 2                     | 0         | 0               | 16  |
| McPhee                         | 2      | 2        | 10     | 2                         | 0                | 0                     | 0         | 0               | 16  |
| Kelly                          | 15     | 0        | 0      | 0                         | 5                | 0                     | 0         | 0               | 20  |
| Panorama                       | 0      | 0        | 0      | 3                         | 0                | 0                     | 0         | 0               | 3   |
| Northeast Kelly                | 6      | 0        | 0      | 0                         | 0                | 0                     | 0         | 0               | 6   |
| Mount Elsie                    | 8      | 0        | 0      | 0                         | 2                | 0                     | 0         | 0               | 10  |
|                                |        |          |        |                           |                  |                       |           |                 |     |
| Duffer Formation in Marble Bar |        |          |        |                           |                  |                       |           |                 |     |
|                                | 8      | 9        | 11     | 2                         | 0                | 0                     | 0         | 0               | 30  |

Table 3.1: Total of spectra from the metamorphic dataset which have chlorite as most dominant mineral

The samples were used for preparing thin sections for optical, and electron microscopy. The thin sections were carbon coated, to avoid charging effects in the electron microprobe. These thin sections were studied under optical microscope in plane polarized and crossed polarized light to get a better understanding of the mineral composition and compare this with the interpretation of the mineral composition from the spectra. Areas containing chlorite were marked to make it easy to find these areas under the electron microprobe.

The electron microprobe analysis itself was performed with the JEOL JXA-8530F HyperProbe Field Emission gun with a 15kV beam current.

## 3.4 Chemical analysis

The microprobe measurements are used to calculate the cation abundancy of the chlorites. For the cation calculation the method of Foster (1962) is used (see figure 3.4) Our data did not contain information about the oxidation state of iron so it was assumed that all iron measured was ferric iron. Because chlorite is an hydrated mineral, it was

not possible estimate the ferrous iron content by normalizing the oxide measurements to 100%.



Figure 3.4: Method for calculating cation abundancy in chlorites from Foster (1962)

## 3.5 Data interpretation

Data interpretation was done by using Matlab for comparing measurements and preparing plots. ArcGIS was used for spatial analysis. Interpolation between data points for the alteration dataset was done with the nearest neighbour function in ArcGIS (Childs, 2004). The details of the absorption features were calculated with the minwav function in HypPy after a convex hull substraction (Bakker and Oosthoek).

## 4 Results

## 4.1 Mineral assemblage from spectral data interpretation

The bar diagram in figure 4.1 shows results of the mineral assemblage interpretation from the reflection spectra. The y-axis shows the relative abundance of minerals which are classified as most dominant. The rock types as classified by Smithies (2007), who used the rock nomenclature of IUGS classicication (Le Maitre et al., 2005), are ranked from most mafic on the left to felsic on the right For the alteration dataset the chloritequartz and sericite alteration types are grouped.



Figure 4.1: Most dominant minerals in reflection spectra as ratio per alteration or rock type. Numbers indicate the amount of spectra per group.

The samples from the alteration dataset which were sampled in the alteration zone were plotted on the map from Brauhart et al. (1998). Samples which were collected on the granite complex are not shown on this graph. Some chlorite-quartz and sericite alterations types were grouped in the map. The samples from Smithies (2007) are not plotted in a map because these are collected on multiple location and is more difficult to capture the mineral distribution in one map.



Figure 4.2: Alteration map from Brauhart et al. (1998) and data points of the samples where chlorite is noticed in the spectrum. The first and second dominant minerals from the spectral mineral interpretation are grouped. Cross symbols indicate the locations of the volcanogenic massive sulfide deposits

## 4.2 Mineral assemblage from optical microscopy

The result of the microscopy mineral interpretation is shown in Table 4.1. Percentages were estimations of the abundance in the thin sections. Minerals marked with a asterisk are minerals which are measured with the electron microprobe but were not visible or could not be classified under the optical microscope.

|   | Bas  | salt  |   |
|---|--|---|---|
| 715   | 717  | 725   | 766   |
| Calcite (10%)<br>Chlorite (30%)<br>Matrix (50%)<br>Opaque minerals<br>(10%)<br>Magnetite*                 | Chlorite (44%)<br>Matrix (44%)<br>Epidote (2%)<br>Opaque minerals<br>(10%)<br>Amphibole*<br>Orthoclaso*  | Chlorite (40%)<br>Matrix (30%)<br>Epidote (2%)<br>Opaque minerals<br>(8%)<br>Quartz (20%<br>Amphibolo*  | Amphibole(87%)<br>Matrix (10%)<br>Chlorite (3%)<br>Calcite<br>Clinopyroxene<br>Albito*  |
| Epidote*  | Titanite*  | Orthoclase*<br>Titanite*  | ADIte   |
|   | And  | esite   |   |
| 704   | 718  | 720   | 722   |
| Calcite (1%)<br>Chlorite (14%)<br>Matrix (85%)<br>Mica (muscovite)*<br>Albite*<br>Zircon*                 | Mica (8%)<br>Chlorite (15%)<br>Epidote (5%)<br>Opaque minerals<br>(2%)<br>Quartz (10%)<br>Matrix (60%)<br>Clinopyroxene*<br>Titanite*<br>Orthoclase*<br>Calcite* | Feldspar (30%)<br>Chlorite (15%)<br>Quartz (10%)<br>Matrix (43%)<br>Mica(2%)<br>Epidote*<br>Copper pyrite*<br>Albite<br>Sphelerite*<br>Muscovite* | Quartz (10%)<br>Chlorite (40%)<br>Epidote (5%)<br>Opaque mineral<br>(10%)<br>Matrix (30%)<br>Mica (5%)<br>Titanite*<br>Rutile*<br>Magnetite*<br>Spinel* |
| 708   | 711  | 716   |   |
| Feldspar (20%)<br>Chlorite (10%)<br>Epidote (2%)<br>Opaque minerals<br>(15%)<br>Matrix (51%)<br>Mica (2%) | Feldspar (30%)<br>Chlorite (10%)<br>Epidote (2%)<br>Opaque minerals<br>(3%)<br>Matrix (55%)<br>Titanite*   | Feldspar (30%)<br>Chlorite (10%)<br>Calcite (10%)<br>Epidote (2%)<br>Matrix (40%)<br>Opaque minerals<br>(8%)                                      |   |

|  | Rhyolite  |  |  |  |  |  |
|--|---|--|--|--|--|--|
| 724  | 726   |  |  |  |  |  |
| Feldspar (30%)<br>Chlorite (5%)<br>Epidote (5%)<br>Opaque minerals<br>(5%)<br>Matrix (30%)<br>Mica (15%)<br>Quartz (20%) | Feldspar (20%)<br>Quartz (70%)<br>Chlorite (5%)<br>Calcite (5%) |  |  |  |  |  |

Table 4.1: Mineral assemblage according to the microscopy studies. Percentages are estimations of the abundance in the thin sections.

## 4.3 Chlorite composition analysis

To get an idea what type of chlorites have formed in these rocks and which substitution reactions play a role in the chemical composition, some scatter plots were made to study relation in cation abundance. All graphs were made for both the metamorphic and alteration dataset which are shown in respectively red triangles and blue dots.

## 4.3.1 Fe-Mg substitution

Figure 4.3 is a scatter plot of the iron and magnesium cations in the octahedral sheet of chlorite. This done to see if there is any linear trend between cations on the x- and y-axis, the R-square value shows the goodness of fit. R-square is a value between 0 and 1 where the numbers closer to one indicates a better linear correlation.



Figure 4.3: Scatter plot of the iron and magnesium cations on respectively the x- and y-axis. Left graph, red triangles are data from the metamorphic dataset and right graph, blue dots from the alteration dataset.

## 4.3.2 Dioctahedral-Trioctahedral substitution

Figure 4.4 shows the scatter plot with octahedral aluminium, and iron plus magnesium on respectively the y- and x-axis. Again a trendline with corresponding R-square value.



Figure 4.4: Scatter plot of octahedral aluminium and iron plus magnesium cations on respectively the y- and x-axis. Left graph, red triangles are data from the metamorphic dataset and right graph, blue dots from the alteration dataset.

#### 4.3.3 Tschermak substitution

The plot of the tschermak substitution shows cations of total aluminium in both octahedral as tetrahedral sheet on the y-axis and silicium, iron and magnesium on the x-axis.



Figure 4.5: Scatter plot of the total aluminium and a sum of silicium, iron and magnesium the y- and x-axis. Left graph, red triangles are data from the metamorphic dataset and right graph, blue dots from the alteration dataset.

## 4.4 Bulk rock composition collected samples

From the beginning it was assumed that the samples collected for the metamorphic, and alteration dataset were respectively altered and non-altered. To test if this is correct the data from the X-ray fluorescence measurements were plotted in a so called alteration boxplot. This scatter plot is described by Large et al. (2001). The results are shown in figure 4.6. For the alteration datasets the data are grouped by their type of alteration, for the metamorphic dataset this is done by the rock classification.

The boxes in the middle of the graph shows where all non-altered rocks should plot, and the black dots including labels where some minerals would be plotted in the graph. The x-axis shows the Ishikawa alteration index and y-axis the chlorite-carbonate-pyrite index. Formulas are found below.

$$AI = \frac{100(K_2O + MgO)}{K_2O + MgO + Na_2O + CaO}$$
(1)

$$CCPI = \frac{100(MgO + FeO)}{MgO + FeO + K_2O + Na_2O}$$
(2)



Figure 4.6: Alteration boxplot as described by Large et al. (2001) for the metamorphic dataset (above) and alteration dataset (below).

An AFM-diagram was plotted (see figure 4.7) to see if the bulk rock composition data show a trend which can be linked to fractionation of a magma series. The data plotted are from the X-ray fluorescence measurements.



Figure 4.7: AFM-diagram with magnesium, ferrous iron, sodium and potassium oxides from the X-ray fluorescence measurements.

## 4.5 Chlorite absorption features

The influence of chlorite composition on the reflection spectra was tested with scatter plots including trend line with corresponding R-square values. The trendline was made for the samples which have chlorite as most dominant mineral (filled symbols). Data of the characteristic absorption features were plotted in figure 4.8 and 4.9 with the magnesium number.

Boxplots were made to test if there is a difference in absorption wavelengths between the rock types or alteration zones. For the alteration dataset two sets of boxplots were made for lithology and ateration facies. The metamorphic dataset was compared with lithology.



Figure 4.8: Wavelength of the characteristic absorption features of chlorite and the magnesium number of chlorite.



Figure 4.9: Absorption depths of the characteristic absorption features of chlorite and the magnesium number of chlorite.



Figure 4.10: Boxplots with the absorption wavelengths of the rocktypes from the metamorphic dataset. The middle line in the box shows the median and the lower and upper box boundaries are respectively the first and third quartile. The whiskers show the minimum or maximum unless one of the datapoints plot out of the 1.5 times the interquartile range (Q1-Q3) below Q1 or above Q3, than the datapoint is shown as outlier with an asterisk.



Figure 4.11: Boxplots with the absorption wavelengths of the rocktypes and alteration facies from the alteration dataset. The middle line in the box shows the median and the lower and upper box boundaries are respectively the first and third quartile. The whiskers show the minimum or maximum unless one of the datapoints plot out of the 1.5 times the inter-quartile range (Q1-Q3) below Q1 or above Q3, than the datapoint is shown as outlier with an asterisk.

#### 4.6 Magnesium number variation

The variation of magnesium number in chlorite is compared with the magnesium number from the bulk rock composition. The magnesium number is calculated with the oxides from the microprobe measurements and data from X-ray fluorescence.



Figure 4.12: Scatter plot of the magnesium numbers of XRF(y-axis) and Microprobe (x-axis) for both alteration as metamorphic dataset

Figure 4.13 shows the result of natural neighbour interpolation. This interpolation was done between all data points for every characteristic absorption feature of chlorite. The interpolation map in Figure 4.13 was clipped in ArcGIS so only the result of the interpolation within the alteration zones and not of the Strelley granite.



Figure 4.13: Result of the nearest neighbor interpolation in ArcGIS between all samples for all characteristic absorption wavelengths of chlorite.

## 5 Discussion

## 5.1 Mineral composition

The mineral interpretation from the reflection spectrum shows us that chlorite, white mica and amphibole are the most dominant minerals in the reflection spectra from this part of the Pilbara Craton samples in both the metamorphic and alteration datasets. The mineral assemblage of the alteration dataset shows most variation between the chlorite-quartz and sericite alteration zones. Samples with background alteration have almost equal amounts of chlorite and white mica dominant in their spectra.

The spectral mineral interpretation of the alteration dataset shows some similarities with the typical mineral assemblage of the different alteration facies from Brauhart et al. (1998) (see Table 5.1). However, not all samples in this column have characteristic absorption features in the spectral range studied. The minerals which are recognizable in the spectra which are chlorite and sericite are both present in the background alteration facies, and that chlorite is in the typical assemblage of chlorite-quartz alteration and sericite in both sericite-quartz as feldspar-sericite-quartz.

Spectral studies carried out by of Huston et al. (1999) and van Ruitenbeek et al. (2006) also noticed the high abundance of chlorite and sericite in the spectra and both used the ratios of the 2200nm and 2250nm to map the abundance of chlorite and sericite in the area. The white mica probability map of van Ruitenbeek et al. (2006)shows a similar result with our data points in figure 4.2. The light and dark green dots on the map in figure 4.2, which indicate the samples with chlorite as most dominant mineral, plot in the area with low white mica probability. This plot also shows us that if chlorite is not found as most dominant mineral it is often found as secondary mineral in the spectrum. Additional information in which belt and rock type chlorite is found as most dominant mineral can be seen in the Appendix.

| Alteration<br>facies             | Typical assemblage  | Host rocks  | Variations on typical alter-<br>ation assemblage   |
|----------------------------------|---|---|--|
| Background                       | (Albite and/or K<br>feldspar)-chlorite<br>(ankerite and/or<br>calcite)-quartz-pyrite<br>$\pm$ leucoxene $\pm$ mag-<br>netite $\pm$ sericite | All unites  | (1)Epidote- actinolite-<br>background alteration in<br>some mafic- intermediate<br>intrusion(2) albite-bearing<br>with no K feldspar; de-<br>veloped at the top of the<br>outer phase granite and<br>base of the volcanic pile |
| Feldspar-<br>sericite-<br>quartz | (K felsspar and/or<br>albite)-sericite-<br>quartz-ankerite-<br>leucoxene± pyrite  | Mainly felsic vol-<br>canic rocks but<br>some andesite-<br>basalt | (1) K feldspar beraring<br>with no albite and only<br>minor sericite; (2) transi-<br>tional to background  |
| Sericite-<br>quartz              | Quartz-sericite-<br>leucoxene $\pm$ ankerite<br>$\pm$ pyrite  | Felsic volcanic<br>rocks or granite                               | (1) Greisen-style alter-<br>ation in the granite; (2)<br>transitional to background  |
| Chlorite-<br>quartz              | Quartz-chlorite-<br>sericite $\pm$ leucoxene<br>$\pm$ hematite  | All units   | (1) Chlorite-quartz-<br>ankerite alteration (2)<br>transitional to back-<br>ground   |

Table 5.1: Interpretation of Brauhart et al. (1998) of the different alteration facies including typical mineral assemblage.

The mineral assemblage variates with the rock type where amphibole is found in the (ultra-)mafic rocks, chlorite in intermediate and white mica in felsic rocks. This succession can be explained since it is known that the rocks are metamorphosed till greenschist and some to amphibolite facies (Smithies, 2007). Amphibole is a common mineral in mafic, metamorphic rocks. Chlorite can be formed during metamorphic processes by a reaction of feldspar and pyroxene which are common minerals in basalt and andesite rocks. White micas are formed as reaction product in the more felsic rocks which are dominated by quartz and feldspar. So all these minerals are interpreted as a product of low-grade metamorphism in volcanic rocks. Mineral structures in the thin sections indicated that the rock was unstable and secondary minerals replaced primary minerals and others minerals like quartz recrystallized.

Petrography provides us the opportunity to verify our spectral mineral composition interpretation of the metamorphic dataset. From the thirteen thin sections only one sample had a significant amount of amphibole (87%) and minor chlorite (3%) which is a similar result as the spectral interpretation. The trend that chlorite is more abundant in mafic rocks than felsic rocks was also observed in the thin sections. The abundance of mica was in all thin sections really low with a maximum of 15% in the rhyolite sample 724. Because all samples where really fine grained it was hard to quantify mineral abundances. Especially for the classification of calcite and mica this was hard since both minerals have high birefringe in cross-polarized light and other features like relief or twinning were not visible in minerals with low grain size. For example in sample 726 it is possible that some of the minerals interpreted as calcite are actually micas. The reflection spectra of the rhyolite samples are more flat than the other samples, it is thought that this is due to an higher abundance of minerals without characteristic absorption features in NIR like feldspar and quartz. Sometimes the minerals were to small for classification and were like a matrix between other minerals in the thin section. Based on the birefringe in cross polarized light this was probably a combination of quartz and feldspar, so not recognizable in the spectra. Combination of the spectral data with the microscopy study can be found in the appendix.

## 5.2 Chlorite classification

The analysis of the cation abundance of chlorites show that all chlorites are trioctahedral which means they have at least 10 cations in the octahedral sheet. The plots made to study the substitution reactions show a good fit with the linear trend line. For the Fe-Mg substitution some data points plot away from the trend line, but it seems that the closer the samples plot to zero magnesium and iron the more octahedral aluminium was present in the sample. This variation in aluminium content is also visible in the di-tri octahedral plot where the metamorphic dataset has three samples which have an higher Al(VI) content and these are the three outliers from the Fe-Mg substitution. The alteration dataset shows three samples with at least four aluminium cations in the octahedral sheet and a clustering of samples near four aluminium cations. Also for the alteration dataset a trend was observed where the samples from closer to 0,0 in Fe-Mg scatter plot, plot higher in the di-tri substitution graph. These outliers also exist in plot of tschermak substitution. So besides a few samples which have more aluminium in octahedral sheet the variation in iron and magnesium have a good linear correlation. The total amount of octahedral iron and magnesium is again well correlated with octahedral aluminium. As long as iron and magnesium are perfectly correlated there is a good correlation in tschermak substitution. Aluminium iron and magnesium are the most dominant cations in the octahedral sheet.

## 5.3 Bulk rock composition

The plots with the X-ray fluorescence data make it plausible that the alteration dataset indeed contains altered samples and the metamorphic dataset mainly non-altered. This conclusion comes from the alteration boxplots and the AFM ternary plot.

The metamorphic dataset shows a nice trend in the alteration boxplot where most felsic minerals plot in the lower left corner and the more mafic the sample the higher the chlorite-carbonate-pyrite index (CCPI) (Large et al., 2001). In total seven samples in the lower right corner do not fit in the general trend from the other samples, and this was interpreted as altered rock by Abweny (2012).

Data from the alteration dataset show a totally different pattern than the data from the metamorphic dataset. The background alteration data have a wide variation in the plot but the other alteration types have a better clustering. All chlorite-quartz zones plot in the upper right corner and have an high CCPI and Ishikawa alteration index (AI).

Feldspar and sericite alteration types do not have a good clustering but in general they plot in the lower right corner where sericite should plot according to Large et al. (2001).

The AFM ternary plot supports that the metamorphic dataset has mainly non-altered samples. The data show a nice trend which is similar to a tholeiitic magma series which fits with the observations of Smithies (2007). This tholeiitic trend does not exist in the alteration dataset. This is expected since Brauhart et al. (2001) described the enrichment and depletion of elements in different alteration zones. This changed the bulk rock composition which resulted in a different trend in the AFM-diagram



Figure 5.1: Tholeiitic and calalkaline magma series in AFM ternary diagram

## 5.4 Absorption features

In figure 4.8 the correlation between absorption wavelengths with magnesium number is studied with a scatter plot. All trend lines show a decrease in wavelength with an increase of the magnesium number. However there are some differences in goodness of fit between the different absorption features. In both datasets the MgOH absorption features shows best correlation with the wavelength. The trend line and R-square values were calculated for the data where chlorite is the most dominant mineral in the spectrum (e.g. filled data points).

It is striking in the data from the metamorphic dataset that samples with chlorite as secondary mineral do not have the expected correlation with the magnesium number. Sample 724 which has a magnesium number around 0.55 and extremely low and high FeOH and MgOH absorption features does not fit in any of the trends. The high magnesium number cannot be explained with an high magnesium number in the bulk rock composition. It was thought that the sample would be the outlier in the Fe-Mg substitution plot but this is not the case, so the composition of this chlorite mineral does not contain more octahedral aluminium than other samples. Also the spectrum does not show any indications of other minerals influencing the spectrum besides white mica and chlorite. According the alteration boxplot it is unlikely that this mineral is influenced by hydrothermal alteration processes. Although there are no indicators for other minerals than chlorite and white mica it is still possible that another mineral has influenced the spectrum. As described in the literature review there are minerals like epidote and carbonate which have similar absorption features as chlorite. These minerals are not uncommon in greenstone belts and can be are also noticed in the thin sections. The problem with chlorite, epidote and calcite mixtures was studied by Dalton et al. (2004) who eventually measured multiple reference spectra from known mixtures of chlorite, epidote, and calcite. A more detailed study with these reference spectra might solve questions about the influence of secondary spectra.

The alteration dataset has multiple points which plot below the trend line, indicated with the black line. A closer look on these samples shows us that all of these samples have a low quality spectrum which is difficult to determine a minimum wavelength. An example of one of the spectra which was marked as low-quality is shown in figure 5.2. Without these samples we still see a better fit of the absorption wavelength. The OH absorption near 1400 has a good trend with hydroxyl as well. The data of the alteration dataset shows that the spectra where chlorite is interpreted as secondary sample is still usable to get an indication of the magnesium number.



Figure 5.2: Spectrum 207498 which is one of the outliers in the alteration dataset for the wavelength/magnesium number plot

One of the samples from the metamorphic dataset was selected for the microprobe study to test if amphibole has any effect on the MgOH absorption feature. This was investigated since Abweny (2012) concluded that the low wavelength near 2350nm was a result of low magnesium number of chlorite which could be correlated to metamorphism in amphibolite facies. In the scatter plots it can be seen that the samples indicated as amphibole have a relatively good fit for the 2250 and 1400nm absorption features but this is extremely low for the MgOH absorption feature. This feature is shared with amphibole spectrum and supports the assumption that amphibole in the spectrum lowers the wavelength near 2350nm. So the conclusion of Abweny (2012) that the MgOH absorption feature can be used to indicate metamorphic facies is only partly correct. The amphibolite facies can be recognized by the MgOH absorption feature but this is due to the presence of amphibole and not due to the low magnesium number in chlorite. This means that the amphibolite facies can only be characterized if the rock is (ultra-)mafic, because that is where amphibole forms when a rock enters the amphibolite facies. More data from chlorite is necessary to support this conclusion and to make sure this measurement is not one of the outliers.

Besides the wavelengths also the data with absorption depths of the features is plotted (see Figure 4.9), but none of the data showed a good correlation with the wavelength. Some of the data from the metamorphic dataset shows some trend but the goodness of fit is, so low that it is not useful for this study. It is assumed that secondary minerals have too much influence on the absorption depths that it is not correlated with the magnesium number. Doublier et al. (2012) compared the depth of the absorption features with the metamorphic grade, estimated from ratios calculated from X-ray diffraction measurements. This was done on pelites and it was emphasized that it could be more problematic for mafic rocks which have more secondary minerals like epidote and amphibole. Some boxplots were made with the absorption wavelengths to see what could have caused the difference in magnesium numbers in chlorites. For the metamorphic dataset the rock types are ranked from mafic on the left to felsic on the right. We see a general trend from lower wavelength in the mafic rocks to higher wavelengths in the felsic rocks. This trend is less visible in the FeOH absorption feature but we have seen in earlier plot that the correlation is less good than for example OH and MgOH. This trend is not visible in the alteration dataset but this was not expected because of earlier observations which showed that the rocks composition is changed due to alteration processes. However the alteration types do not show any significant differences either.

Because both bulk rock and chlorite composition were determined, a plot is made to compare both ratios of iron and magnesium oxides. As can be seen there is an almost perfect 1:1 trend between the microprobe data and data from the X-ray fluorescense. This means that most of the time chlorite has a similar composition with respect to magnesium and iron as the bulk rock. This correlation was also noticed by Shikazono and Kawahata (1987).

Because the boxplot of the alteration dataset did not show a clear and understandable result it is decided to do a spatial analysis in ArcGIS. All samples are plotted and an interpolation is made between the samples and the wavelength number. The MgOH feature shows most details which is interesting because this had the best fit with the magnesium number. This data is compared with a study of Brauhart et al. (2001) and shows some similarities. Brauhart et al. (2001) has made maps which shows some absolute mass transfer of different elements in the bulk rock. Figure 5.4 show the maps of  $Fe_2O_3$  and MgO. If we compare these maps with the map of the interpolation of the wavelength of MgOH absorption feature some similar patterns are recognizable. Green areas from 4.13 have low wavelengths and so high magnesium content and are under the VHMS deposits. The same pattern is described by Brauhart et al. (2001) that the magnesium and iron is enriched in the transgressive alteration zones. The semiconformable alteration zone between Kangaroo Caves and Sulphur Springs shows some similarities enrichment of magnesium which is also noticed in our interpolation map. Differences between both maps can be described because our data shows a magnesium number and not relative abundance of magnesium or iron. A problem with this



Figure 5.3: Interpretation of fluid paths by using the white mica index from van Ruitenbeek et al. (2005)

approach is that both iron as magnesium are enriched

in transgressive alteration zones under the VHMS deposits so this will not effect the magnesium number which is a ratio between magnesium and iron. The data also show similarities with the interpretation of fluid paths interpreted by van Ruitenbeek et al. (2005). Here we can see that the increase of magnesium number is in the chlorite-quartz discharge zones (see figure 5.3).



Figure 5.4: Absolute mass transfer from Brauhart et al. (2001) of MgO and Fe<sub>2</sub>O<sub>3</sub> in the panorama district. Red is are enriched in the element and blue depleted.

The metamorphic dataset already showed a nice trend with increasing wavelengths towards the more felsic rocks. This means with the correlation with magnesium number that less magnesium is found in the more felsic rocks. Now we know that the magnesium content in chlorite is related to the bulk rock composition we can link this with what was observed from the AFM-diagram. In a tholeiitic magna series the magnesium content decreases later in the magna series. It thus appears that metamorphism did not influence the composition of the chlorite, but that this was inherited from the original tholeiites. Terabayashi et al. (2003) also concluded that metamorphism has a little effect on the chlorite magnesium number. The study with these samples can be repeated by using X-ray diffraction measurements and compare depth of 1900, 2250, or 2350nm features with the Arkai index which is an indicator for metamorphic grade Doublier et al. (2012).

## 6 Conclusions

The estimation of the mineral assemblage showed a lot of similarities with maps made by van Ruitenbeek et al. (2006) and Huston et al. (1999). The interpretation fits with the observations from Brauhart et al. (1998) and our study on the thin sections from the non-altered rocks. This supports that the mineral interpretation and the method were a good estimation of the real rock composition with respect to the minerals which have a characteristic absorption feature in the studied wavelength range.

Measurements from the microprobe indicate that all samples contained tri-octahedral chlorites where the Fe-mg, di-tri, and tschermak substitution were recognized in the plots from the calculated cations. Fe-Mg substitution was the most dominant and only a few of the samples contained more octahedral aluminium.

The Fe-Mg substitution was recognized in the reflection spectra in the NIR wavelength range which showed that the characteristic absorption features are correlated with the magnesium number of chlorite. Besides some outliers the 1400nm OH feature, 2250nm FeOH and 2350nm MgOH feature have a good fit, where MgOH has the best correlation. The depths of the absorption features showed no correlation with the magnesium number. Data from the electron microprobe and X-ray fluorescence showed that the magnesium and iron content are strongly correlated with the abundance in chlorite. Other than the conclusion of Abweny (2012) it is thought that non-altered rocks have this variability due to the tholeiitic magma series and is not due to the metamorphic grade. The study on amphibolite rock indicates that amphibole lowers the absorption wavelength near 2350nm. This makes it possible to classify rocks in the amphibolite facies but only (ultra-)mafic rocks. More felsic rocks do not have amphibole in samples since these only form in mafic rocks.

The altered rocks do not show any tholeiitic trend and also the alteration boxplot indicate that the bulk rock composition of the rocks is changed due to hydrothermal alteration. Just like the non-altered rocks the composition of chlorite with respect to magnesium and iron has a good correlation with the bulk rock composition. An interpolation map of the wavelength of the characteristic absorption features show a pattern which can be correlated with the discharge zones of convection cells near VMS deposits.

# 7 Acknowledgment

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# 8 Appendix

# 8.1 Chlorite interpreted as most dominant mineral in the metamorphic dataset

Sum is the total amount of samples where chlorite was interpreted as most dominant mineral in the spectrum for each formation or rock type. Total indicates the number of samples from the formation or rock type. Ratio is sum divided by total.

|                      | Basalt | Dacite | Komatiite | Andesite | Rhyollite | Komatitic basalt | Periodotite/komatiite | Sum | Total | Ratio |
|----------------------|--------|--------|-----------|----------|-----------|------------------|-----------------------|-----|-------|-------|
| Apex Basalt          | 54     | 0      | 3         | 0        | 0         | 0                | 0                     | 57  | 69    | 0.83  |
| Duffer formation     | 18     | 18     | 0         | 18       | 0         | 0                | 0                     | 54  | 75    | 0.72  |
| North Star Basalt    | 15     | 0      | 0         | 0        | 0         | 3                | 0                     | 18  | 18    | 1.00  |
| Mt Ada Basalt        | 30     | 0      | 0         | 0        | 0         | 6                | 0                     | 36  | 39    | 0.92  |
| Coonterunah Subgroup | 60     | 12     | 0         | 54       | 0         | 0                | 0                     | 126 | 168   | 0.75  |
| Euro Basalt          | 108    | 0      | 0         | 0        | 0         | 27               | 0                     | 135 | 165   | 0.82  |
| Panorama Formation   | 3      | 9      | 0         | 6        | 6         | 0                | 0                     | 24  | 65    | 0.37  |
| Charteris Basalt     | 18     | 0      | 0         | 0        | 0         | 0                | 0                     | 18  | 18    | 1.00  |
|                      |        |        |           |          |           |                  |                       |     |       |       |
| Sum                  | 306    | 39     | 3         | 78       | 6         | 36               | 0                     |     |       |       |
| Total                | 363    | 68     | 18        | 81       | 36        | 45               | 6                     |     |       |       |
| Ratio                | 0.84   | 0.57   | 0.17      | 0.96     | 0.17      | 0.80             | 0.00                  |     |       |       |

# 8.2 Chlorite interpreted as most dominant mineral in the alteration dataset

Sum is the total amount of samples where chlorite was interpreted as most dominant mineral in the spectrum for each formation or rock type. Total indicates the number of samples from the formation or rock type. Ratio is sum divided by total.

|                        | Dacite | Andesite | Andesite-basalt | Rhyolite | Diorite | Dolerite | Equigranular granite | Granophyre | Porphyritic granite | Intermediate hybrid | Hydrothermal vein | Microdiorite | Sum | Total | Ratio |
|------------------------|--------|----------|-----------------|----------|---------|----------|----------------------|------------|---------------------|---------------------|-------------------|--------------|-----|-------|-------|
| None                   | 0      | 0        | 0               | 0        | 0       | 3        | 0                    | 0          | 3                   | 1                   | 0                 | 0            | 7   | 18    | 0.39  |
| Bg                     | 2      | 18       | 48              | 5        | 0       | 0        | 2                    | 7          | 0                   | 0                   | 0                 | 8            | 90  | 171   | 0.53  |
| Fse                    | 0      | 0        | 0               | 1        | 0       | 0        | 0                    | 0          | 0                   | 0                   | 0                 | 0            | 1   | 24    | 0.04  |
| Trans-                 | 2      | 0        | 5               | 0        | 1       | 0        | 0                    | 0          | 0                   | 0                   | 0                 | 0            | 8   | 16    | 0.50  |
| $\mathbf{c}\mathbf{q}$ |        |          |                 |          |         |          |                      |            |                     |                     |                   |              |     |       |       |
| Cq-cb                  | 0      | 0        | 5               | 0        | 0       | 0        | 0                    | 0          | 0                   | 0                   | 0                 | 0            | 5   | 6     | 0.83  |
| Cq                     | 4      | 11       | 58              | 1        | 0       | 0        | 0                    | 1          | 0                   | 0                   | 1                 | 4            | 80  | 116   | 0.69  |
|                        |        |          |                 |          |         |          |                      |            |                     |                     |                   |              |     |       |       |
| Sum                    | 8      | 29       | 116             | 7        | 1       | 3        | 2                    | 8          | 3                   | 1                   | 1                 | 12           |     |       |       |
| Total                  | 42     | 35       | 152             | 37       | 1       | 5        | 24                   | 41         | 8                   | 2                   | 1                 | 25           |     |       |       |
| Ratio                  | 0.19   | 0.83     | 0.76            | 0.19     | 1.00    | 0.60     | 0.08                 | 0.20       | 0.38                | 0.50                | 1.00              | 0.48         |     |       |       |



## 8.3 Spectral information including mineral assemblages



| 704 | Chlorite<br>Sericite | 1404nm/ 1404nm/ 1404nm<br>2255nm/ 2255nm/ 2255nm<br>2340nm/ 2340nm/ 2341nm | Calcite (1%)<br>Chlorite (14%)<br>Matrix (85%)<br>Albite*<br>Zircon*<br>Mica (muscovite)*   |
|-----|----------------------|--|---|
| 718 | Chlorite             | 1398nm/ 1398nm/ 1398nm<br>2254nm/ 2254nm/ 2254nm<br>2335nm/ 2335nm/ 2337nm | Mica (8%)<br>Chlorite (15%)<br>Epidote (5%)<br>Opaque minerals (2%)<br>Quartz (10%)<br>Matrix (60%)<br>Calcite*<br>Clinopyroxene*<br>Titanite*<br>Orthoclase* |
| 720 | Chlorite             | 1401nm/ 1401nm/ 1401nm<br>2256nm/ 2256nm/ 2256nm<br>2339nm/ 2339nm/ 2338nm | Feldspar (30%)<br>Chlorite (15%)<br>Quartz (10%)<br>Matrix (43%)<br>Epidote*<br>Copper pyrite*<br>Albite*<br>Sphalerite*<br>Muscovite*                        |
| 722 | Chlorite             | 1403nm/ 1403nm/ 1403nm<br>2256nm/ 2256nm/ 2256nm<br>2340nm/ 2340nm/ 2340nm | Feldspar (10%)<br>Chlorite (40%)<br>Epidote (5%)<br>Opaque minerals (10%)   |





| 708 | Chlorite | 1409nm/ 1407nm/ 1409nm                                   | Feldspar $(20\%)$        |
|-----|----------|--|--------------------------|
|     | Sericite | 2254nm/ 2255nm/ 2254nm                                   | Chlorite $(10\%)$        |
|     |          | 2342nm/ 2342nm/ 2342nm                                   | Epidote $(2\%)$          |
|     |          |  | Opaque minerals $(15\%)$ |
|     |          |  | Matrix $(51\%)$          |
|     |          |  | Mica $(2\%)$             |
| 711 | Chlorite | $1402 nm/ \ 1401 nm/ \ 1402 nm$                          | Feldspar $(30\%)$        |
|     |          | $2255 \mathrm{nm}/\ 2255 \mathrm{nm}/\ 2255 \mathrm{nm}$ | Chlorite $(10\%)$        |
|     |          | $2339 \mathrm{nm}/\ 2338 \mathrm{nm}/\ 2339 \mathrm{nm}$ | Epidote $(2\%)$          |
|     |          |  | Opaque minerals $(3\%)$  |
|     |          |  | Matrix $(55\%)$          |
|     |          |  | Titanite*                |
| 716 | Chlorite | $1402 \mathrm{nm}/\ 1402 \mathrm{nm}/\ 1403 \mathrm{nm}$ | Feldspar $(30\%)$        |
|     | Epidote  | $2256 \mathrm{nm}/\ 2256 \mathrm{nm}/\ 2256 \mathrm{nm}$ | Chlorite $(10\%)$        |
|     |          | $2339 \mathrm{nm}/\ 2339 \mathrm{nm}/\ 2339 \mathrm{nm}$ | Calcite $(10\%)$         |
|     |          |  | Epidote $(2\%)$          |
|     |          |  | Matrix $(40\%)$          |
|     |          |  | Opaque minerals $(8\%)$  |



| 724 | Sericite<br>Chlorite | 1412nm/ 1412nm/ 1413nm<br>2249nm/ 2249nm/ -<br>2353nm/ 2352nm/ 2351nm      | Feldspar (30%)<br>Chlorite (5%)<br>Epidote (5%)<br>Opaque minerals (5%)<br>Matrix (30%)<br>Mica (15%)<br>Quartz (20%) |
|-----|----------------------|--|---|
| 726 | Sericite<br>Chlorite | 1410nm/ 1408nm/ 1409nm<br>2251nm/ 2253nm/ 2251nm<br>2346nm/ 2253nm/ 2250nm | Feldspar (20%)<br>Chlorite (5%)<br>Calcite (5%)<br>Quartz (70%)   |

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