An investigation of multiphase solid inclusion assemblages inside a garnet websterite sample from Fjørtoft, W. Norway



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# Abstract

Multiphase solid inclusions are found in a garnet websterite from Bardane, Fjørtoft Island, W. Norway. This garnet websterite consists out of large crystals of orthopyroxene + clinopyroxene + garnet + olivine + Cr-spinel and comes from a pod inside an orogenic garnet peridotite body inside a continental gneiss complex. The websterite pod crystallized in original minimal mid-Proterozoic depleted mantle peridotite and got metasomatised during a subsequent Caledonian to Scandian subduction cycle. The subducting slab released COH-rich subduction zone fluids concentrated and along into the slab-mantle interface, responsible for the precipitation of multiphase solid inclusions inside the primary minerals. Previous work on a garnet websterite from the same peridotite body in Bardane indicated the presence of microdiamonds in multiphase solid inclusions giving evidence for UHP (>130 km) deep subduction. A comparison with this previously studied garnet websterite will be made with an in-situ garnet websterite to confirm the presence of in-situ microdiamonds in multiphase solid inclusions.

Back-scattered electron SEM images have identified multiphase solid inclusions with mineral assemblages of phlogopite, BaMg-carbonate, dolomite, magnesite, Cl-apatite, monazite, rutile, Cr-spinel (Cr#=58-91), (Fe,Ni,Cu) sulfides and elemental C inside M2 orthopyroxene and clinopyroxene crystals. This means introduction of at least the elements C, K, Ti, Ba, Cl, P, Ni, Cu, S, Nb, La, Ce and H<sub>2</sub>O by pervasive subduction zone fluids. Inclusions in M2 spinel grains (Cr#=55) contain OH-apatite, orthopyroxene, clinopyroxene and Al-oxides.

Several elemental carbon inclusions in orthopyroxene and clinopyroxene have an euhedral shape similar to those already identified as microdiamonds in the previously studied websterite. The current study unfortunately lacks Raman confirmation to positively identify the carbon inclusions as microdiamonds, but taken the similarities between the two websterites into account it is very likely that the euhedral shaped carbon inclusions found in this study are microdiamonds or are graphitized microdiamonds. Electron microprobe data confirmed the similarities between the two garnet websterites by elemental wt. % oxide analysis where the chemical compositions of the main M2 minerals are within 1 wt. % oxide difference from each other.

The high occurrence of elemental carbon in the multiphase solid inclusions gives evidence for a reducing character of the subduction zone fluid, although there is also a fair amount of carbonate present in the multiphase assemblages. Oxygen fugacity was therefore not high enough to break up all carbonate.

This leads to the conclusion that the subduction zone fluid was an immiscible Csaturated C-O-H-, silicate- and sulfide-rich (supercritical) fluid. Where LILE, HFSE and LREE were released from the subducting slab by dehydration and decarbonization reactions, forming fluids rich in solutes which were pervasive and precipitated inside recrystallizing minerals as MSI (in the garnet websterite) in a reducing environment. Table of contents

1	Introduction		4
т.		ll Sigh processing cubduction	4
	1.1. Ulua-i		4
	1.2. P-1 pa	un	5
~			6
2.	Geological I	history	6
3.	Methods		7
4.	Oxygen fug	acity	8
	4.1. Diamo	nd formation	8
5.	Subduction	zone fluids	9
	5.1. Aqueo	us fluids and hydrous melts	9
	5.2. Second	d critical endpoint	11
	5.3. Hydrou	us minerals	11
	5.4. Nomin	ally anhydrous minerals	11
6.	Mineral che	mistry	12
	6.1. Orthog	byroxene	12
	6.2. Clinop	vroxene	13
	6.3. Garnet	-	17
	6.4. Spinel		19
	6.5. Phlogo	nite	24
	6.6 Multin	nase solid inclusions	26
7	Discussion		34
<i>'</i> .		n fugacity	34
	7.1. Oxyge	nase solid inclusion assemblages	34
	7.2. Multipl	ase solu inclusion assemblages	27
0	7.5. Carbon	Idles	2/
0.	Acknowlode	amonto.	20
9.	Acknowledg	Jements	29
10.	Annendia		39
11.	Appendix	<b>T</b>	42
	11.1.	lables	42
		11, 12, 13	42
		T4, T5, T6	43
		17	44
		T8	45
		T9, T10	46
	11.2.	Thin sections and study locations – BSE images	47
		Thin section 1	47
		Thin section 2	50
		Thin section 3	52
		Thin section 4	56
		Thin section 5	64
		Thin section 6	69
	11.3.	Extra BSE images – Spectra	72
	11.4.	Thin section sample locations from 62 Fjørtoft 1	75
	<b>TTTTT</b>		, 5

Cover: A contrast colored BSE image of a M3A spinel grain (orange/yellow) at location 6-13, surrounded by symplectite (dark blue), inside a garnet grain (light blue) with multiphase solid inclusions in the spinel visible as the nearly vertical green (~10  $\mu$ m long) colored rod in the black square in the spinel grain.

## 1.Introduction

Garnet websterites have been collected from an orogenic peridotite lens inside high grade continental gneisses from Bardane, Fjørtoft island, Western Gneiss Region (WGR) Norway (figure 1). The discovery of microdiamonds as a stable phase inside multiphase solid inclusion assemblages (MSI) in these garnet websterites has been reported by van Roermund et al. (2002). The diamonds are present in a megacrystic garnet websterite sample extracted from a small pod ( $<0,5 \text{ m}^3$ ) of deformed and partly recrystallized garnet websterite within a small outcrop (20-25 m lens) of interlayered garnet-bearing and garnet-free peridotite (Carswell and van Roermund, 2005; Brueckner et al., 2002). The first discovery of microdiamonds is made in a websterite with original high Ca-Al orthopyroxene megacrysts, up to ~20 cm original size, which contain exsolution patterns of clinopyroxene and garnet. In this study a comparison is made between the garnet websterite found as a loose block and studied by van Roermund et al. (2002) and Carswell and van Roermund (2005), and a garnet websterite collected in-situ from the same peridotite lens, the latter consist of smaller primary minerals, up to ~3 cm in size, of clinopyroxene, orthopyroxene and garnet which contains considerably higher modal amounts of clinopyroxene (~13 vol.%). The aim of this study is to confirm the occurrence of microdiamonds which implicates a subduction depth of >130 km and to find similar MSI assemblages as reported by van Roermund et al. (2002) & Carswell and van Roermund (2005).

## 1.1 Ultra-high pressure subduction

Microdiamonds in the continental garnet-kyanite-biotite paragneisses of the Western Gneiss region (WGR) in Norway have been discovered since the Geological Survey of Norway started an investigation for the possible occurrence of microdiamonds in 1992 (Dobrzhinetskaya et al., 1995). Microdiamonds in subduction zones are not widespread around the globe and they have been found in the Dabie/Sulu region, China (Xu et al., 2003), Kokchetav Massif, Kazachstan, the Erzgebirge, Germany (Stöckhert et al., 2001), and regions in Greece, Italy, Morocco, Indonesia, Czech Republic and Vietnam (Dobrzhinetskaya et al., 2003; Frezzotti et al., 2011; Schertl and Sobolev, 2013 and references therein). Of which the WGR, the Kokchetav Massif and the Dabie/Sulu regions are well known ultra-high pressure (UHP) metamorphic terranes (van Roermund and Drury, 1998; Schertl and Sobolev, 2013; Malaspina et al., 2006). Regional metamorphism above the coesite/quartz transition line is called UHP, below that line it is called high pressure (HP) metamorphism. Almost all UHP metamorphic zones which contain diamonds are formed at convergent plate boundaries in Paleozoic-Mesozoic times (480-250 Ma) (Dobrzhinetskaya, 2012). Usually microdiamonds are found in metasedimentary rocks (gneisses), eclogites and/or garnet peridotites. The aim of this study is a garnet websterite inside an orogenic garnet peridotite lens found at Fjørtoft (figure 1).



The occurrence of microdiamonds (Dobrzhinetskaya et al., 1995), discovery of coesite



(Smith, 1984; Wain, 1997) and the presence of relict Majoritic garnet microstructures (van Roermund and Drury, 1998; van Roermund et al., 2000; Spengler et al., 2009; Scambelluri et al., 2008; Scambelluri et al., 2010) gives compelling evidence for the presence of an exhumed deep-subducted continental collision zone in the UHP zone of the WGR, which is believed to went up to 150-200 km in depth (Scambelluri et al., 2008; Scambelluri et al., 2009). Continental subduction to these depths in this area was previously also implied by van Roermund et al. (2002) who argued that the associated ultra-high pressure and relatively moderate UHP temperatures occurred during prograde continental subduction associated with solid-state recrystallization of the garnet websterite. Together with the trace elements and isotopic data presented by Brueckner et al. (2002) provided solid evidence for cold continental lithospheric subduction as a result of the Scandian collision between Baltica and Laurentia.

## 1.2 P-T path

The garnet websterites form pods inside high-temperature upwellings of Archean former transition zone mantle, characterized by incompatible element-depletion, due to partial melting. In the decompression process refractory peridotites are left behind (350 km;stage M1A, figure 2) which eventually accreted into a thick cratonic lithosphere in the garnetolivine stability field (stage M1B, figure 2) in Archean times (Scambelluri et al., 2008; Van Roermund 2009; Scambelluri et al., 2010; Drury and van Roermund 1998; Spengler et al., 2006). Isobaric cooling to 1000-1300°C until the Mid-Proterozoic marks stage M2 during which the garnet websterite pods were formed (Brueckner et al., 2002) with a mineral assemblage of coarse garnet + orthopyroxene + clinopyroxene  $\pm$  olivine  $\pm$  Cr-spinel (Cr#=70). A subsequent Caledonian/Scandian (430-390 Ma) subduction cycle (stage M3), when Baltica underthrusted Laurentia, took the mantle rocks down to deeper parts of the supra-subduction mantle wedge where Scandian fluids infiltrated and metasomatised the overhanging mantle rocks and initiated diamond crystallization (Figure 2, P-T path; figure 3, visualization) (Malaspina et al., 2010; Scambelluri et al., 2008). Peak M3 mineral assemblages consist of (majoritic) garnet + orthopyroxene + olivine  $\pm$  clinopyroxene  $\pm$ phlogopite  $\pm$  carbonates  $\pm$  spinel (Cr#=55) and characterized by much smaller grain sizes than the M2 assemblage and even later stage M3 generation of spinel grains from M1 and M2 garnet break-down products growing into symplectite have Cr#<40 (see figure 2A) (Carswell and van Roermund, 2005; van Roermund 2009). The M1, M2, M3 classification used in this study will refer to the one used by van Roermund (2009) and Scambelluri et al. (2008).

Presence of phlogopite constrains temperature and pressure in the M3 stage to a maximum of 1200°C and 7 GPa where phlogopite is still stable and which is well inside the diamond stability field (Scambelluri et al., 2008). The combined presence of phlogopite and carbonates already suggests that the M3 exsolution lamellae are subduction fluid derived. Peak metamorphic conditions determined with M3 orthopyroxene in pyroxenites from Otrøy give maximum UHP conditions of 6.34 GPa and 872°C (Spengler et al., 2009). Microdiamond inclusions entrapped in spinel inside M3 garnet formed minimal around 4 GPa and 840-900 °C. The M3 stage is here the moment in time that the multiphase inclusions were formed and where combined assemblages of carbonate + phlogopite + carbon are present as has been reported by Carswell and van Roermund (2005).



#### 1.3 Multiphase solid inclusions

The multiphase solid inclusions (MSI) in the websterite from Bardane were first found and described by van Roermund et al. (2002) and Carswell and van Roermund (2005). Similar polyphase inclusions have also been found in the Dabie-Sulu region and described by Malaspina et al. (2006). Both terranes form exhumed continental subduction zones and the MSI in the rocks are interpreted to have formed by precipitaton from fluids percolating through the slab during subduction. The MSI in the host minerals are representations of the mobile elements in- and precipitated minerals from subduction fluids. The UHP minerals coesite, diamond and majoritic garnet can trap MSI which indicates that they were included as supercritical fluids at UHP conditions (Zheng and Hermann, 2014). UHP terrains are mainly composed of supracrustal rocks which contain index minerals at the micron scale which are indicative for the UHP conditions. These inclusions are often found in chemically and mechanically resistant minerals like spinel, zircon and garnet (Liou et al., 2004). Previous studies on Bardane garnet websterites (van Roermund et al., 2002; Carswell and van Roermund, 2005) have shown that polyphase inclusions are present in garnet, spinel and orthopyroxene, and the MSI in these minerals will be the focus of this study. The composition of the MSI in the different minerals in this study will be indicative for the composition of the subduction zone fluids during the time of precipitation of the minerals. Identification of elements related to and hence an approximation of the composition of the subduction zone fluids will be a focus of this study. MSI assemblages will be examined for differences in assemblages and therefore a potential different timing of fluid introduction and accompanying variation in composition of the subduction zone fluids.



Figure 3. Path of the mantle derived garnet peridotites introduced into the subducting Baltica slab beneath Laurentia (after Clos et al., 2014).

## 2. Geological history

A continent-continent collision initiates subduction of one plate underneath the other plate and, for the WGR, subduct to depths where it temporarily resides into the diamond stability field (>130 km depth or >3.8 GPA), where UHP metamorphism takes place before the buoyant subducted continental crust is exhumed to the surface. In the WGR the overriding plate is the Laurentian plate and the subducting plate is the basement of Baltica and its overlying Vendian to Early Paleozoic cover (Terry et al., 2000a). Both collided due to the closing of the Iapetus Ocean. During the Scandian orogenic event an Archaean lithospheric mantle-derived peridotite body with its megacrystic garnet, high aluminous two pyroxene Proterozoic websterite assemblage (M1) was introduced into the westwards subducting continental crustal gneiss complex (Carswell and van Roermund, 2005; van Roermund and Drury 1998). The orogenic peridotites at the island of Otrøy (close to Fjørtoft) enclosed in Baltica basement gneisses have recorded a residence time of ca. 25 Ma in the diamond stability field and ca. 30 Ma in the coesite stability field with a peak depth of 200 km (Spengler et al., 2009). Previously a residence time of 15 Ma with peak subduction depths of 120-125 km was estimated using modelled exhumation rates for the WGR (i.a. Terry et al., 2000b; Kylander-Clark et al., 2008).

The island of Fjørtoft is part of Nørdoyane, an island group, in the north western part of the WGR, Norway (figure 1). The geology of Fjørtoft is characterized by the regionally correlated kyanite eclogites inside the Blåhø Nappe (figure 1) which are associated with the microdiamond-bearing rocks on the northeast coast of Fjørtoft (Dobrzhinetskaya et al., 1995; Terry et al., 2000a). Geochronological, thermobarometric and microstructural evidence lead to the conclusion that the peridotite lens on Bardane, Fjørtoft and the kyanite eclogites of the Blåhø Nappe underwent simultaneously UHP metamorphism during the Scandian (430-390 Ma) (Carswell et al., 2006).

Deformation events resulting from the Scandian orogeny and dehydration of minerals in the subducting slab introduced metasomatic (COH) fluids enriched in carbon and other incompatible elements into the subducting slab around and during peak metamorphic conditions. Intense deformation of the subducted slab created pathways for the crust derived COH-rich fluids to enter the websterites and simultaneously metasomatised the peridotite body during deformation (Brueckner et al., 2002; Spengler et al., 2009).

Coherent exhumation of the subducted slab in the WGR with an exhumation rate of ~7 mm/yr involved local partial melting during the higher pressure parts of the PT-path (Kylander-Clarck et al., 2008). Exhumation of the WGR was nearly isothermally from the crust-mantle transition zone to shallow crustal levels (Zheng, 2012). The residence time of the subducted slab determined by Spengler et al. (2009) is longer than generally accepted for exhumed UHP metamorphic terranes, but comparable to other large exhumed UHP provinces like the Dabie-Sulu region (Kylander-Clark et al., 2008).

#### 3. Methods

The locations of MSI in the collected rocks are not visible with the naked eye and therefore there is no prior location where a known high abundancy of MSI will be. So choosing a rock slice of which thin sections are made is arbitrary and finding good examples of MSI is bounded by the occurrence of MSI in the sampled thin sections. Six thin sections (30  $\mu$ m thick) numbered 1 to 6 were made from a single rock slice in the central part of the in-situ websterite pod, called 62 Fjørtoft 1 (figure 4), parallel to each other (see appendix 11.4 for locations and appendix 11.2 for scans of the thin sections). The thin sections were polished with an aluminum-oxide (Al<sub>2</sub>O<sub>3</sub>) polishing agent. The samples have been studied optically and after that the samples were coated with carbon for study using the SEM FEG XL-30. The thin sections were imaged using the BSE detector of the 30  $\mu$ m thick thin sections. This in turn has led to the complication that optically identified inclusions were not always found in the SEM FEG XL-30, as they appeared to be below the surface.

The location numbers used in this study have the following structure. For example the location 4-12-2 is situated in thin section 4 (4-12-2) at study area 12 (4-12-2) at MSI 2 in



Figure 4. A slice of the garnet websterite pod, called 62 Fjørtoft 1. The polished surface is the study surface. Six thin sections are made from left to right numbered 1 to 6; the rectangles roughly show the sample locations of the thin sections (see appendix 11.4).

the study area (4-12-**2**). The numbers represent layers of focus, where the first numbers contains the thin section, the second number is a broad area between 50-200 micron and an eventual third number indicates the encountered MSI assemblages in this broad area, of which the largest is about 15 micron.

Spot analyses were made with the SEM FEG XL-30, using an EDS device for identification and analyses of the mineral compositions. The composition of the main minerals has been measured with higher accuracy on the Electron Microprobe (EM), compared to the analyses with the SEM FEG XL-30 (semi quantitative analysis with ~10% error). Cathode Luminescence (CL) was used in an attempt to identify carbon polymorphs and CL-maps have been made from the different sulfides. CL was used because van Roermund et al. (2002) identified microdiamonds with CL in their study as well as Raman spectrometry. Raman spectrometry analysis is used in this study to identify the carbon polymorph present in MSI assemblages. The standard diamond peak has a high intensity band at 1332 cm<sup>-1</sup>, any shift from this peak may results from deformation of the diamond lattice, instrumental uncertainties or the presence of point defects (Dobrzhinetskaya et al., 2006) Image analysis gave the relative rock mineral modal abundances in percentage.

#### 4. Oxygen fugacity

Oxygen fugacity ( $fO_2$ ) is a variable which is used to describe the oxygen chemical potential ( $\mu O_2$ ). It is a way to quantify the redox state of a system in which oxygen for a certain amount takes part in chemical reactions and can control the stability of mineral assemblages (Malaspina et al., 2009). The oxidation state of a system is expressed in terms of the  $fO_2$  relative to buffer reactions such as the fayalite, magnesite, quartz system (FMQ: forsterite +  $O_2$  = magnesite + quartz), the iron wüstite system (IW: iron +  $O_2$  = wüstite) or the magnetite hematite system (MH: magnetite +  $O_2$  = hematite).

Malaspina and Tumiati (2012) determined oxygen fugacity ( $fO_2$ ) values for the Bardane garnet peridotite which are 0.5 to 1.5 log units higher ( $\Delta$ FMQ of -2–0) than for garnet peridotites from other geological settings, such as cratonic xenoliths, when equilibrated at similar pressures. The trend for orogenic garnet peridotites from the Ulten zone (Italian Central Alps), Dabie-Sulu zone and Bardane is a decreasing oxygen fugacity ( $fO_2$ ), and thus a more reducing environment, with increasing pressure. A reducing environment can cause oxygen to leave the system which in turn would lead to break up of chemical compounds which contain oxygen, like carbonate ( $CO_3$ ), and leave a higher concentration behind of elements they were bounded to, like C.

The composition of C-saturated COH fluids in the deep mantle is closely related to the oxidation state of the system, where ferric ( $Fe^{3+}$ ) and ferrous ( $Fe^{2+}$ ) iron in mineral assemblages can buffer the  $fO_2$  of the system and thus the COH fluid speciation (Malaspina et al., 2010). Garnet is commonly used as a mineral in which the  $Fe^{3+}/\Sigma Fe$  ratio is used to determine the oxygen fugacity ( $fO_2$ ) of a system. The M3 majoritic garnets from Bardane record a decrease in  $Fe^{3+}/\Sigma Fe$  ratio from core to rim (Malaspina and Tumiati, 2012) and thus a decrease in  $O_2$ -content which in turn could be the result of a reducing environment during metasomatism. Although it is also concluded by Malaspina et al. (2012) that an increase in  $Fe^{3+}/\Sigma Fe$  ratio in garnet does not necessarily correspond to an enrichment in  $O_2$  (and vice versa). Also there are other mineral phases in metasomatised garnet peridotites which incorporate  $Fe^{3+}$ ; phlogopite, amphibole, olivine, spinel, orthopyroxene and clinopyroxene. So the  $Fe^{3+}$  content and zonation of these minerals has to be considered in order to make reliable quantifications on the oxygen fugacity of the bulk rock.

#### 4.1 Diamond formation

An evaluation of 225 peridotite xenolith samples of deep cratonic lithosphere has indicated that the last fluids were of a reducing nature (Stachel and Luth, 2015). Sulfide melts (Fe-S-O) in the deep mantle are a potential reducing agent for carbonate in the deep mantle. Experiments at 6-7.5 GPa and 1300°C, conducted by Gunn an Luth (2006), produced graphite at these conditions. Reduction of carbonate is one possible way to acquire carbon for diamonds to form. A relevant reaction for the stability of carbonate in peridotitic material is known as EMOD or EMOG (depending on the carbon polymorph produced): enstatite + magnesite = forsterite + diamond/graphite + O<sub>2</sub> (Gunn and Luth, 2006). Recrystallization of graphite is another way to form diamond on higher pressures. This requires graphite to be already present in the rock at the onset of subduction. This is not very likely, because carbon minerals are only found in MSI rather than as a single phase. The third possibility for accumulation of carbon is precipitation from fluids. This would also be in a reducing environment with decreasing  $fO_2$  as otherwise free carbon in solution

would form carbonate and no carbon would accumulate. An oversaturated C-bearing fluid would have the capability to precipitate carbon (Malaspina and Tumiati, 2012).

For the Bardane websterites a reducing environment is required, due to the decreasing  $fO_2$  conditions. Because carbon does not occur as a single phase, but with other C-bearing phases (e.g. carbonates) it is likely to have originated from carbonates during metasomatism under increasing reducing environment which liberated the carbon from the carbonates.

#### 5. Subduction zone fluids

Volatile elements at the slab mantle interface in subduction zones are transported by fluid phases (aqueous fluids, hydrous silicate melts or solute-rich supercritical fluids) which are enriched in COH components derived by decarbonation, dehydration and/or partial melting (Malaspina et al., 2010; Hermann et al., 2006). Characterization of subduction zone fluids provides insight in the processes where subduction zone fluids are derived from and/or are involved in. Most of what is known about composition and element mobility of subduction zone fluids is derived from oceanic subduction zones (Spandler and Pirard, 2013) and there is less knowledge available about continental subduction zone fluids and element mobility. However, in more recent times more studies have focussed on this subject (Shatsky et al., 2015; Zheng and Hermann, 2014; Zhao et al., 2007). Knowing the composition of continental subduction zone fluids gives a better understanding of element recycling and mantle evolution. Subduction zone fluids are the carriers of incompatible elements like the large ion lithophile elements (LILE) Cs, Rb, Sr, Ba, K, Pb, B, As, and Sb, the high field strength elements (HFSE) P, Ti, Nb, Ta, Th, U, Zr and Hf, and the rare earth elements (REE) (Spandler and Pirard, 2013; Hermann and Rubatto, 2014). The kind of elements transported by subduction zone fluids depends on the kind of fluid it is transported in. LILE are easily dissolved in aqueous fluids where (L)REE are not easily dissolved in aqueous fluids. Light rare earth elements (LREE) (and in small amounts also heavy rare earth elements (HREE)) are preferentially transported by hydrous melts (figure 5) and fluids above the second critical endpoint (supercritical fluids), leaving a HREE enrichment in the residue (Zheng and Hermann, 2014). For the HFSE, U and Nb are more enriched in the fluid phase compared to Th and Ta, where rutile is the host for Nb, Ta and Ti and Zircon is the host for U, apatite is the major host for P (Zheng and Hermann, 2014). Dehydration experiments on mafic oceanic crust conducted by Green and Adam (2003) provided good evidence for trace element partitioning in fluids. Experiments at conditions of 650-700°C and 30 kbar showed that a large amount of LILE and Sr enter the aqueous solution, while REE, Th, U and other HFSE are contained in the residue. P-T conditions for the Bardane websterites are well above these experimental values (peak values of 1200°C and 7 GPa) and it is therefore assumable that more than one fluid phase have existed throughout the evolution of the subduction zone besides only an aqueous fluid phase.

Subducted sediments on top of the slab (in particularly pelites (Hermann and Spandler, 2008)) are the main key reservoir for LREE, LILE, Th and U and they play an important role in the transport of these elements from the subducting slab to the depleted mantle wedge (Hermann et al., 2006). The sediment cover on an oceanic slab is relatively small compared to the sediment cover of a continental slab, and thus the amount of trace elements present during metasomatism in a continental subduction zone is also higher. Through studies of stable isotopes, fluid inclusion and petrological phase relationships in UHP metamorphism it has become clear that compositional differences between continental and oceanic subducted crusts will result in differences in the mobility and/or amount of elements dissolved in aqueous fluid (Zheng, 2009).

The Bardane rocks have LREE enriched M3 clinopyroxene and M2 orthopyroxene whereas the M3-2 and M3-3 garnet show LREE depleted patterns or flat REE patterns depending on (majoritic) garnet measurement with pyroxene needles (flat REE) or garnet measurement without pyroxene needles (LREE depleted). LILE depletion in the pyroxenes and garnet is associated with a high LILE content in phlogopite (up to 1000xPM=Primitive Mantle), although the LILE present in these minerals are different from each other (Carswell and van Roermund, 2005; Scambelluri et al., 2010 and figures therein).

#### 5.1 Aqueous fluids and hydrous melts

The most important source for water in subduction zones is the breakdown of hydrous minerals, where the breakdown of anhydrous minerals provides an additional water source (Zheng and Hermann, 2014). These water sources can accumulate (on grain boundaries) and induce partial melting to produce a hydrous melt, depending on the amount of dissolved solutes. Fluids in HP and UHP rocks always coexist with a solid residue and the



Figure 5. Experimentally determined element distribution patterns in hydrous melts and aqueous fluids in HP to UHP conditions. The higher amount of solutes in hydrous melts is visible (after Zheng and Hermann, 2014).

amount of dissolved solutes is buffered by the surrounding rock. An aqueous fluid is a water-rich fluid phase which consists out of less than ~30 wt.% of solutes and a hydrous melt is a fluid phase which consists out of more than ~65 wt.% of solutes (Hermann et al., 2006). Zheng and Hermann (2014) experimentally determined the concentration of the major and trace elements in HP and UHP aqueous fluids and hydrous melts (figure 5). The higher amount of solutes in hydrous melts with respect to aqueous fluids becomes evident in this figure. Aqueous melts are preferentially enriched in LILE and have relatively flat REE patterns whereas hydrous melts have a slight enrichment in LILE and are relatively LREE enriched. There is an overall HREE enrichment in the residue as these elements do not

tend to enter hydrous melts and aqueous fluids. There are two types of metasomatism recognized in orogenic 1) modal metasomatism peridotite where hydrous minerals like amphibole and phlogopite are generated and where mineralogical changes occur in the orogenic peridotite. 2) The second metasomatism is cryptic type of metasomatism where enrichment of water-soluble elements like LILE and LREE, without mineralogical changes of the peridotite is characteristic (Zheng, 2012). Modal metasomatism is further characterised by the growth of the new mineral phases serpentine, chlorite, amphibole, phlogopite, apatite, carbonate, sulphide, titanite, ilmenite and zircon (Zheng and Hermann, 2014). These minerals are not originally present in the depleted mantle peridotite and are thus indicators for addition of elements for the growth of these minerals by subduction zone fluids on the slab-mantle interface.





## 5.2 Second critical endpoint

The second critical endpoint of a fluid phase is strongly dependent on the protolith and composition of the participating phases (figure 6). Different compositions will inhibit a different (wet) solidus and therefore different bulk rock compositions will affect the nature of the fluid phase. A single fluid phase occurring above its second critical endpoint is called a supercritical fluid. The wet solidus separates the two immiscible phases (e.g. aqueous fluid and hydrous melt) until it reaches the second critical endpoint, towards which the two fluid phases become progressively miscible with increasing pressure (Zheng and Hermann, 2014). At this point the phases become a supercritical- or miscible single-phase where the amount of solutes in the supercritical fluids varies as a function of pressure and temperature (Hack et al., 2007). Figure 6 shows the second critical endpoint of peridotite and it is evident that the peak M3 conditions (6.34 GPa and 872°C) are above the second critical endpoint and a supercritical fluid is present. Coexistence of multiple types of minerals in MSI (e.g. anhydrous, hydrous and salt minerals) indicates that the MSI precipitated from a supercritical fluid instead of an aqueous fluid or hydrous melt (Zheng et al., 2011). Properties of a hydrous melt and an aqueous fluid become miscible above the second critical endpoint and a wet solidus is no longer present. Fluids above the second critical endpoint become transitional fluids where a dramatic increase in solutes occurs from aqueous fluids to hydrous melts. From this point on a fluid with continuously evolving physical and chemical properties with temperature is present and can either exist as a supercritical hydrous melt or supercritical aqueous fluid (Hermann et al., 2006). An aqueous fluid which dissolves minerals in the subsolidus region will continuously dissolve minerals in the supercritical region when the critical curve is crossed. These supercritical fluids are assumed to be less-dense and less-viscous than water-saturated hydrous melts and thus have the potential to migrate upwards (Hack et al., 2007), which makes them more prone to penetrate overlying rocks.

#### 5.3 Hydrous minerals

Phengite is a hydrous mineral which breaks down experimentally at UHP and 800-1000 °C which leads to partial melting of subducted crust. Amphibole (glaucophane, hornblende) and mica (white mica and biotite) are important hydrous minerals in pre-eclogite facies rocks, but in subduction zones phengite is the most important hydrous mineral in felsic UHP crust because it is a stable mineral at these pressures (Hermann and Rubatto, 2014; Schmidt and Poli, 2003). Although other hydrous phases besides phengite can still occur in minor amounts at these depths as mineral inclusions or in allanite-quartz veins, examples are reported from the Dabie-Sulu orogenic belt (Zheng, 2009 and references therein). Epidote (allanite, epidote, zoisite) is also an important hydrous mineral group which can dehydrate at subduction pressure and temperature conditions (Zheng et al., 2011). Common reactions to liberate water during prograde metamorphism under eclogite-facies conditions are the breakdown of paragonite, amphibole, lawsonite, zoisite and breakdown of amphibole and zoisite combined (Zheng, 2009).

#### 5.4 Nominally anhydrous minerals

Pyroxene, garnet, olivine, quartz and rutile are nominally anhydrous minerals where pyroxenes typically contain ~200-500 ppm  $H_2O$  and garnets and olivine contains ~1-50 ppm  $H_2O$  in which the hydrogen is structurally bound as hydroxyl (OH) (Bell and Rossman, 1992). More recent results on  $H_2O$  concentrations in garnets from the Dabie-Sulu orogenic belt show concentrations of up to ~1800 ppm  $H_2O$  (Zheng, 2009 and references therein). This shows that there are significant amounts of structurally bound hydroxyl present in nominally anhydrous minerals, although in the same minerals there can also be molecular  $H_2O$  present in surface and volume defects (Zheng and Hermann 2014 and references therein). Water content can also increase with increasing pressure, a linear increase in  $H_2O$  content with pressure has been observed in garnet and omphacite in an eclogite from the Kokchetav massif (Katayama et al., 2006).

Currently subduction usually takes place at low geotherms 5-10°C/km where a high pressure has to be obtained before nominally anhydrous minerals will start to dehydrate. For this reason it is possible for dehydration reactions to take place at subarc depths (>80 km) in continental subduction zones, in contradiction to oceanic subduction where a hot geotherm is present and dehydration reactions take place at shallower depths (<80km) (Zheng and Hermann, 2014).

## 6. Mineral chemistry

The garnet websterite consists out of orthopyroxene (~60 vol.%), garnet (~20 vol.%), clinopyroxene (~13 vol.%), olivine (~5 vol.%), spinel (<1 vol.%) and phlogopite (<1 vol.%), with accessory carbon polymorphs, carbonates, (Fe, Ni, Cu) sulphides, rutile, apatite and monazite. Representative mineral compositions are given in table 1, other analyses are given in appendix 11.1 – tables.

## 6.1 Orthopyroxene

The modal volume the of websterite occupied by ~60%. orthopyroxene is Orthopyroxene can be expressed in terms of the endmembers Wollastonite (Ca2Si2O6), Ferrosilite  $(Fe_2Si_2O_6)$  and Enstatite  $(Mg_2Si_2O_6)$ . The FEG SEM XL-30 and EMP results of orthopyroxene analyses measured in this study are presented in figure 8, table 1, 2 & 3, where it becomes evident that orthopyroxenes in the Barda ne garnet websterite is a Mgrich enstatite with Mg#= 90-96. Semi-quantitative analyses on the FEG SEM XL-30 (green and red points) give a similar range of compositions comparable to the composition of M2 orthopyroxene

Table 1.	Representative	microprobe	analyses.

Mineral phase	M3 Grt	М2 Орх	М2 Срх	M2 Sp	M3 Phl
Sample no.	6-13	6-20-11	6-20-11	6-13	4-15
Location	Core	Core	Core	Core	Core
Oxide wt. %					
SiO2	41.89	57.71	55.07	0.03	55.78
TiO2	0.06	0.01	0.08	0.27	0.30
AI2O3	21.39	0.99	3.67	25.11	1.18
FeO	7.89	4.67	1.54	15.02	4.81
MnO	0.43	0.11	0.07	0.03	0.12
MgO	20.75	36.28	15.43	13.73	34.81
CaO	4.65	0.18	20.12	0.01	0.15
Na2O	0.02	0.01	2.61	0.00	0.03
K2O	0.00	0.00	0.01	0.00	0.56
NiO	0.01	0.09	0.02	0.08	0.05
Cr2O3	3.50	0.32	1.77	45.62	0.7803
Total	100.59	100.36	100.39	99.89	98.56





Figure 8. Orthopyroxene endmember diagram, red, green and black points are FEG SEM XL-30 EDS analysis data points, where red is composition of orthopyroxene in MSI, green is composition of the M2 orthopyroxene mega-crysts and black is composition of orthopyroxene in symplectite. The yellow point is composition of orthopyroxene measured by the Electron Microprobe. Fj-1-34 host opx and Fj-29 corona opx is data from Carswell and van Roermund (2005), F151C-2 M2 opx and F89 M1 opx is data from van Roermund et al. (2002)

measured by the microprobe (yellow point) (analysis results in table 1). There is some difference in composition of orthopyroxene in MSI and the M2 orthopyroxene mega-crysts, which is emphasized by a higher  $AI_2O_3$  content in MSI (figure 7, appendix 11.1 - T4, T5) There is however one MSI measurement which is slightly more enriched in Ca than other measurements. This orthopyroxene inclusion is measured in clinopyroxene exsolution lamellae inside a M2 orthopyroxene next to CI-apatite inclusions. The presence of Ca-rich clinopyroxene can be the reason that a higher than usual Ca content is measured in this orthopyroxene inclusion as it can be a background detection of clinopyroxene. Striking is that the composition of this data point is roughly equal to the composition of M1 orthopyroxene measured by van Roermund et al (2002). The orthopyroxene composition measured in symplectite (black point in figure 8, table



Figure 9. Location 6-13, symplectite between M2 spinel and M3 garnet. The dark mineral in symplectite is orthopyroxene, the lighter mineral clinopyroxene and the lightest mineral is spinel.

2) shows enrichment in Mg (Mg#=96) compared to the other orthopyroxene compositions (Mg#= 90-94) (table 3). This suggests less participation of Fe in orthopyroxene during the formation of the symplectite (see figure 9) with the reaction Grt + Sp<sub>1</sub>  $\rightarrow$  Opx + Cpx + Sp<sub>2</sub> (1) (see figure 9). The Fe content in Sp<sub>2</sub> (wt.% FeO=9.28) is lower than in Sp<sub>1</sub> (wt.% FeO=11.30), so there is less iron incorporated in spinel formed in the symplectite as compared to M2 spinel grains.

	6-13 Opx in symplectite	4-10 M2 Opx core analysis
Wt.% oxide		
MgO	36.48	34.24
$AI_2O_3$	2.66	1.61
SiO <sub>2</sub>	57.34	58.42
FeO	2.45	5.73
Total	100	100

Table 2. SEM XL-30 analyses on orthopyroxene

	М2 Орх	M2 Opx	Opx symplectite	Opx MSI		
Sample no.	4-10	6-20-11	6-13	3-19		
Location	Core	Core	Core	Core		
Anal. method	SEM XL-30	EMP	SEM XL-30	SEM XL-30		
Wt.% oxide						
MgO	34.24	36.28	36.48	36.45		
FeO	5.73	4.67	2.45	6.41		
Mg#	91.4	93.3	96.4	91.0		
Table 2 Differences in Matt of authors may an different anisin						

Table 3. Difference in Mg# of orthopyroxene for different origin

#### 6.2 Clinopyroxene

The modal volume of the websterite occupied by clinopyroxene is ~13 vol.%. Clinopyroxene can be expressed in terms of the endmembers diopside (CaMgSi<sub>2</sub>O<sub>6</sub>), jadeite (NaAlSi<sub>2</sub>O<sub>6</sub>) and aegerine (NaFeSi<sub>2</sub>O<sub>6</sub>). All clinopyroxene measured in this study has a diopside composition (figure 10). The semi-quantitative measurements of the clinopyroxene lamellae, MSI and M2 crystals (green, orange and red points; appendix 11.1 T3, T4, T5) plot roughly on the same position in the endmember diagram (figure 10). The Electron Microprobe data points for the M2 clinopyroxene and the clinopyroxene lamellae (inside the M2 orthopyroxene) also plot in this cluster and all data points show a slight enrichment in Al compared to Fe. The one point which stands out is de clinopyroxene in symplectite which is relatively low on Ca and Mg and enriched in Al compared to other

clinopyroxene compositions. It is possible that the lower Mg content in the symplectite clinopyroxene is related to the higher Mg content of orthopyroxene in symplectite. This would suggest that Mg is preferentially incorporated in enstatitic orthopyroxene rather than diopsidic clinopyroxene during the formation of symplectites which causes the clinopyroxene to obtain a more jadeite (or less diopside) composition compared to other clinopyroxene in the websterite. This is also shown in figure 13 where a clearly higher amount of Al in clinopyroxene in symplectite is shown compared to other clinopyroxene compositions.

Figures 11-15 show the major elements measured in clinopyroxene. Figure 11 shows that Al is independent of the varying amount of Si, and Electron Microprobe data shows that the clinopyroxene M2 grains have a slightly higher Si content than the clinopyroxene lamellae.



Jadeite NaAlSi<sub>2</sub>O<sub>6</sub>

Aegerine NaFeSi<sub>2</sub>O<sub>6</sub>

Figure 10. Clinopyroxene endmember diagram, red, green, orange and black are FEG SEM XL-30 data analysis points, where red is composition of M2 clinopyroxene, green is composition of clinopyroxene lamellae, orange is composition of clinopyroxene in MSI and black is composition of clinopyroxene in symplectite. Yellow and purple are compositions measured by the Electron Microprobe, where yellow is composition of M2 clinopyroxene and purple is composition of clinopyroxene lamellae. Fj-1-31 inside host opx, Fj-1-cpx 2core A3 corona cpx and Fj-1-17 inside host opx is data from van Roermund et al. (2002), F151C-2 M2 cpx is data from Carswell and Van Roermund (2005).

Furthermore it is also visible that clinopyroxene in symplecite has a higher Al content than other clinopyroxene compositions. Figure 12 shows that Na does not significantly change compared to Ca. There is not a clear trend visible in the amount of Na compared to Ca between the different clinopyroxene. The Electron Microprobe data gives higher values for Ca (see appendix 11.1 - T1, T4), which can be the result of higher accuracy measurements. The clinopyroxene in symplectite is slightly enriched in Na and has lower Ca content which was already suggested by the clinopyroxene endmember diagram.

Figure 13 shows that the amount of Ca varies more than Al in all clinopyroxene measurements, although the clinopyroxene in the symplectite is richer in Al than clinopyroxene in M2 grains, MSI and lamellae. The electron microprobe data show a slight depletion of Al in the clinopyroxene lamellae compared to the M2 clinopyroxene grains.

Figure 14 shows a relation between Ca and Mg where the variation in the datacloud is roughly the same for Ca and Mg (which is about 0,2). Again the clinopyroxene in the symplectite has deviating values from the other data points and has a Ca enrichment and Mg depletion.



Figure 12. Na vs. Ca composition of clinopyroxene measured by FEG SEM XL-30 EDS and Electron Microprobe. The Electron Microprobe data has slightly higher Ca (a.p.f.u.), but the data plots roughly in the same cluster. The black diamond represents clinopyroxene in symplectite, the orange diamond is measured in a clinopyroxene lamellae.



Figure 14. Ca vs.Mg composition of clinopyroxene measured by FEG SEM XL-30 EDS and Electron Microprobe. The electron Microprobe data shows slightly higher Mg (a.p.f.u.) compared to the SEM XL-30 data. But data points plot roughly in the same cloud, except the clinopyroxene measured in symplectite and a clinopyroxene measured in a MSI assemblage. These data points have a lower Mg (a.p.f.u.) content.



Figure 15. Cr vs. Al in clinopyroxene measured by FEG SEM XL-30 EDS and Electron Microprobe. The amount of Al (a.p.f.u.) remains fairly constant where the amount of Cr (a.p.f.u.) changes slightly. Especially the difference in microprobe data between clinopyroxene grains and clinopyroxene lamellae stands out. The black diamond represents clinopyroxene in symplectite, the orange diamond is measured in a clinopyroxene lamellae.

Figure 15 shows an interesting relationship between Cr and Al in the different clinopyroxenes. The Al content stays roughly constant and the Cr content varies relatively more. The difference in Cr content (measured by the microprobe, see appendix 11.1 - T1) between the clinopyroxene lamellae, which is higher with 2.69 wt.% oxide  $Cr_2O_3$ , and the clinopyroxene M2 grains, which is lower with 1.77 wt.% oxide  $Cr_2O_3$ , suggests more availability of Cr during the formation of the M3 clinopyroxene lamellae than during the formation of the M2 clinopyroxene. The clinopyroxene in symplectite has a relatively low Cr content, possible due to the simultaneously formation of spinel in the symplectite which could have incorporated more Cr than clinopyroxene, and here again is visible that there is a higher Al content.

Overall the measurements made by the microprobe have an accuracy of  $\pm$  1% for the clinopyroxene data, and measurements made by the SEM XL-30 for the clinopyroxene data is an accuracy of  $\pm$  6%.

### 6.3 Garnet

Garnet composition can be expressed in terms of the endmembers pyrope  $[Mg_3(AI,Cr)_2Si_3O_{12}]$ , grossular  $[Ca_3AI_2Si_3O_{10}]$  and almandine + spessartine  $[(Fe,Mn)_3AI_2Si_3O_{12}]$ . Figure 16 shows that M3 garnet in the Bardane websterite is dominantly pyrope (~60%) in composition and they have relatively high Cr values, 3.50 wt.% Cr<sub>2</sub>O<sub>3</sub>, and a Cr#= 10-13 (see appendix 11.1 – T6). Carswell and van Roermund (2005) determined Cr#=11 for Archean M1 garnet in the megacryst assemblage. So far they are the only ones who published a Cr# for the Bardane garnet and the determined Cr# for garnet in this study can only be compared with this published number.

The microdiamond inclusions have been found for the first time by van Roermund et al. (2002) in M3 garnets which enclosed spinel grains (Cr#= 55) which contained the MSI assemblages. Figure 17 shows a negative correlation between total Fe ( $\Sigma$ Fe) and Mg for the SEM XL-30 data with a similar variation in  $\Sigma$ Fe and Mg which can be attributed to the inaccuracy of the SEM XL-30. The microprobe data shows consistent values. The same issue might cause a slightly wrong representation of the endmember diagram in figure 16, where instead of Fe<sup>2+</sup> total FeO is used to plot the data. Malaspina et al. (2010)



established a negative correlation for the M3 garnets from Bardane and this is associated with a negative correlation between  $Fe^{3+}$  and  $Fe^{2+}$ . This is consistent with a change in the iron oxidation state. It was not possible to make a distinction between  $Fe^{2+}$  and  $Fe^{3+}$ 



during measurements in this study, because both SEM XL-30 and the microprobe only measure total FeO values. So assumptions on the iron oxidation state of the Bardane garnets based on total Fe ( $\Sigma$ Fe) content Mg (a.p.f.u.) versus measurements of the SEM XL-30 and the microprobe cannot be compared with certainty with data from Malaspina et al. (2010). Figure 16 shows the total  $Cr_2O_3$  wt.% versus the CaO wt.% content. There is a positive correlation between the increase in Ca and Cr content based on the SEM XL-30 data, but taken the accuracy of the SEM XL-30 into account this positive correlation can also be the result of that. Although if the effect is due to

inaccuracy, than the scatter of the points is expected to be more randomly distributed than the positive trend shown in figure 18. The composition of garnet is dominantly pyrope (~60%) and an increase in Ca and Cr content will take the composition more to the grossular side of the endmember diagram. Simultaneously a lower total Fe content is accompanied with a slight increase in Al content. Al combined there is no significant difference between the composition of garnet in the Bardane websterite, but some distinctions can be made between the garnets using the elements Mg, ( $\Sigma$ Fe), Cr and Ca, based on the SEM analyses. This needs to be verified by the EMP in a more extensive study since the microprobe data in this study is measured on one garnet grain only.

#### 6.4 Spinel

Spinel is abundant on the microscale (in occurrence, not in vol. %) and is a common mineral in MSI. Figure 19 shows the composition of the spinel grains measured by the FEG SEM XL-30 EDS (analyses are in appendix 11.1 - T7). They are subdivided using Cr# [Cr/(Cr+Al)] into M2 spinel with Cr# $\approx$  64-85, M3A spinel with Cr# $\approx$  40-60, and later stage M3B-C spinel with Cr#< 20-35 (following Carswell and van Roermund, 2005; Scambelluri et al., 2008; van Roermund, 2009) and spinel in MSI varying Cr#= 58-91 (spinel Cr# are in appendix 11.1 – T7). Spinel numbers are grouped within a range of 20, because of the semi-quantitative analysis by the FEG SEM XL-30 (illustrated in figure 19). Spinel compositions become increasingly Al-rich from the M2 to M3A spinels (figure 19E). The composition of the spinel in MSI varies between the M2 and M3A spinel Cr# although it is obvious that the MSI Cr# is not derived during the M2 stage, but during the M3 stage. There is a striking difference between spinel grains which have a later stage M3B-C composition and spinel grains which have formed inside MSI. Later stage M3B-C spinel is relatively enriched in Al and spinel in MSI is relatively enriched in Cr (see appendix 11.1 -T7). Assuming that these MSI spinel grains formed during the same stage (M3) but have different Cr<sub>2</sub>O<sub>3</sub> wt.%, 39.67-52.52 wt.% for MSI and 19.97-36.36 wt.% for M3B-C. This suggests that spinel crystallized during different events and with different Cr compositions, provided that the bulk rock compositions are uniform as well as the oxidation grade. Figure 20 shows a similar relationship between spinel in MSI and M3B-C spinel. The M3B-C spinel grains are more enriched in Mg as they have a higher Mg#, but they also have a lower Cr#, and the spinel grains in MSI have slightly lower Mg#, but are enriched in Cr relative to spinel in MSI. M2 spinel grains have a similar Mg# and Cr# trend as the MSI spinel grains with high Cr content and a low Mg content. Some M2 spinel grains are well inside the chromite field due to the high Cr content (Figure 20). In this study a few MSI

spinels were found having the M3A spinel compositional range similar to spinel compositions as measured by van Roermund et al. (2002) containing microdiamonds in multiphase inclusions, which was also in spinel from the M3A stage with Cr#≈ 55. Overall there is a negative correlation between Mg# and Cr# with an increasing trend for the Mg# from the M2 stage to the M3B-C stage (figure 20). During the same stages there is an increasing trend visible in Al content relative to Cr, from relatively low Al content in the M2 stage to a relatively high Al content in the M3B-C stage (figure 19E). The FeO<sup>tot</sup> content in the different spinel grains is slightly enriched in M2 and some MSI spinel grains compared to MgO,  $Al_2O_3$  and  $Cr_2O_3$  content (see figures 22, 23, 24). But there is overlap between spinel from the different stages for the FeO<sup>tot</sup> and MgO plot (figure 24) with only a few outliers from the M2 stage and spinel in MSI. Figure 21 points out a negative trend between MgO and  $Cr_2O_3$  where spinel from the M2 to the M3B-C stage have lower  $Cr_2O_3$ content and have more MgO content. The spinel in MSI has a striking different composition here, the M2, M3A and M3B-C stages plot in a similar trend (besides a few outliers), where the spinel in MSI do not follow this trend, but has a compositional range of ~40-50 wt.% oxide Cr<sub>2</sub>O<sub>3</sub> and ~5-20 wt.% oxide MgO as can be seen in figure 21. Mean compositions for the spinel in different stages of formation is then (all values in wt.% oxide) for M2:  $AI_2O_3$  14.83, FeO 18.68, MgO 11.00,  $Cr_2O_3$  55.49; for M3A:  $AI_2O_3$  26.44, FeO 14.20, MgO 16.24,  $Cr_2O_3$  42.44; for M3B-C:  $Al_2O_3$  40.79, FeO 13.14, MgO 17.27,  $Cr_2O_3$  27.77. With average Cr# for M2, M3A and M3B-C of respectively 71.8, 52.0 and 31.5 (see appendix 11.1 – T7). The increasing amount of  $Al_2O_3$  and simultaneous decreasing amount of  $Cr_2O_3$ from stage M2 to M3B-C stands out (see figures 22 and 23). Exchange between Al<sup>3+</sup> and Cr<sup>3+</sup> during progression of these stages could be a cause of this.

A linescan through a M3A spinel (figure 25; appendix 11.4 – A3) shows depletion in  $Cr_2O_3$ , from ~45 wt.% to ~41 wt.% oxide, an enrichment of  $Al_2O_3$ , from ~25 wt.% oxide to ~30 wt.% oxide, and a small enrichment in MgO, from ~14 wt.% oxide to ~15 wt.% oxide, at the rim of the spinel grain compared to the core. The M3A spinel is surrounded by symplectite and is enclosed inside a M3 garnet grain.



Figure 19. SEM XL-30 analyses of spinel (listed in appendix 11.1 - T7). A) composition of M2 spinel with Cr#= 64-85 B) composition of M3A spinel with Cr#= 40-60 C) composition of later stage M3B-C spinel with Cr#= 20-35 D) composition of spinel in MSI have Cr#= 58-91 E) composition of M2, M3A and M3B-C spinel combined, showing an increase in Al content from M2 spinel to M3B-C spinel, Fj-1-41 spinel in host opx data point after van Roermund et al. (2002).









#### 6.5 Phlogopite

The chemical composition of biotite can be expressed in the following endmember diagram containing phlogopite  $KMg_3AISi_3O_{10}(OH)_2$ , annite  $KFe_3AISi_3O_{10}(OH)_2$  and siderophyllite  $KFe_2Al(Al_2Si_2)O_{10}(OH)_2$  as endmembers. Biotite can be called phlogopite when the Mg# [Mg/(Mg+Fe<sup>tot</sup>)] >0.5 (Tischendorf et al., 2007). The Mg# is between 0.76-0.94 for all measured biotite and can therefore be called phlogopite (analyses are listed in appendix 11.1 – T9). Figure 26 shows that the composition of M3 phlogopites (M3 stage referred to Scambelluri et al., 2008; van Roermund 2009) in the Bardane websterites measured by the SEM XL-30 and the Electron Microprobe results is roughly equal independent on presence of phlogopite in a MSI or in a exsolution lamellae. One data point of phlogopite in MSI is more Mg rich than the other phlogopite compositions, but this can be due to the surrounding orthopyroxene in this inclusion which could have been measured as a background value because of the small size of the phlogopite inclusion. There is no significant difference in composition between phlogopite in MSI and phlogopite in exsolution lamellae, which suggests that they are derived from a similar compositional fluid for the formation of phlogopite. There is however a difference between the SEM XL-30 data and the microprobe data (see appendix 11.1 -T9). Unfortunately only one measuring point of the microprobe data gave a compositional range without background values for the host orthopyroxene and was therefore the only one useable (location 4-15, appendix 11.2). But this analysis plots very close to the experimental data from Fumagalli et al., (2009). In a (Na + K) vs. Si diagram the SEM XL-30 data plot below the microprobe data point which might be due to the lower accuracy of the SEM XL-30 compared to the Electron Microprobe.

An experimental study on the effect of high- and relatively low-pressure conditions on phlogopite by Fumagalli et al. (2009) indicated that the amount of Si increases and Al, K





and Na decreases with increasing pressure, attributed to substitution reactions. Data from Scambelluri et al. (2010) of M3 phlogopite show the same relationship where an increase in Si is accompanied by a decrease in Na + K. Figure 27 shows data from this study on M3 phlogopite where also a negative correlation is visible between Si and Na + K. The single Electron Microprobe data point plots close to the phlogopite data point of Fumagalli et al. (2009) which corresponds to conditions of 5 GPa and 800°C. These conditions are below the determined peak conditions for the M3 stage (6.34 GPa, 872°C (Spengler et al., 2009)), but outside conditions of the M1 and M2 stages (3.0-4.5 GPa, 1300-1500°C and 3.4-4.1GPa, 840-900°C respectively (Brueckner et al., 2002)). This indicates that phlogopite minerals in exsolution lamellae have formed during the M3 stage, but below peak M3 conditions. Phlogopite inclusions in MSI measured with the FEG SEM XL-30 plot at the lower part of the diagram which might indicate different conditions during formation compared to the phlogopite in exsolution lamellae which are slightly above the MSI data points. But this is difficult to correlate with the data from Fumagalli et al. (2009) since there is no direct link between the negative correlation of Si and Na + K and a linear increase in pressure in high resolution, since the values are too far apart from each other. It can only be said that at low resolution there is a correlation between an increase in pressure and a simultaneously increase in Si and decrease in Na + K, since the trend is visible then.



Figure 27. M3 phlogopite data from the FEG SEM XL-30 and Electron Microprobe (analyses in appendix 11.1 - T9). A negative correlation between Si and K + Na is visible. The electron Microprobe data of phlogopite plots close to experimental data points of 5 GPa/800°C from Fumagalli et al. (2009) for phlogopite compositions (i.e. above the diamond stability line in figure 2). The composition of phlogopite in MSI (measured by the FEG SEM XL-30, green diamonds) plots below phlogopite compositions present as exsolution lamellae (blue diamonds).

## 6.6 Multiphase solid inclusions

MSI are found in M2 orthopyroxene, M2 clinopyroxene and M3 clinopyroxene exsolution lamellae and in some of the M3A spinel grains. The solid inclusions are pervasive in the host minerals in which they occur and are not found on grain boundaries or along cracks. No MSI are found in M3A garnet and M3 phlogopite, although rutile needle-like crystals are present in M3 phlogopite as well as not needle-like spinel and rutile (figure 28). The HFSE Nb is found in some of the not needle-like rutile grains (1.51-2.01 wt.% oxide) (see appendix 11.1 – T10). It is known that rutile has the capability of depleting subduction

zone fluids in HFSE even if it is present in small amounts (~0.2 wt.%) (Brenan et al., 1994). HFSE which are not Other uncommon in rutile like Ta, Hf, Zr, U and Th are not detected by either the FEG SEM XL-30 or the Electron Microprobe and might therefore not be a part of the metasomatising fluid. The presence of rutile and spinel grains suggests mobility of Cr and/or Ti. Although it can be clearly seen in figure 28 that spinel and rutile grains form at cracks or along grain boundaries between the host mineral phlogopite and other matrix minerals and this is observed at several locations in the thin sections. Rutile and spinel also appear in later serpentine veins, which have formed during the



exhumation event and therefore rutile and spinel present on grain boundaries of phlogopite and in or adjacent to serpentine veins could have formed accordingly during the exhumation event.

MSI are common in orthopyroxene and appear in different assemblages. Figure 29 shows a histogram in which the frequency of minerals in inclusions are shown. The histogram does not show the different assemblages present in orthopyroxene, but instead which minerals are common in MSI in orthopyroxene. Clinopyroxene is the most frequently found in MSI and is present in almost all inclusions, which can be expected since the M3 stage is a.o.



Figure 29. Histogram showing the frequency (not vol. %) of all MSI in orthopyroxene. The vertical bars do not represent volume percentage of minerals. Clinopyroxene is most frequently found, carbon and the different carbonates (calcite/dolomite/magnesite/BaMg carbonate) are also frequently found followed by spinel and phlogopite inclusion. Less frequent are Cl-apatite, monazite, rutile, sulphides, coesite, Al-oxide, moissanite and BaAl-silicate.

characterized by the occurrence of many clinopyroxene exsolution lamellae inside M2 orthopyroxene and visible with the optical microscope. Scambelluri et al. (2010) attribute the presence of clinopyroxene in orthopyroxene to the reaction dolomite + orthopyroxene = magnesite + clinopyroxene (2) which started at the onset of the M3 Scandian subduction (named M3-1 by Scambelluri (2010)) and was accompanied by fluid infiltration responsible for the formation of dolomite. This would imply frequent occurrence of magnesite, but this mineral is not frequently found in MSI in orthopyroxene. The most frequently present carbonate in MSI is dolomite, followed shortly by a BaMg-carbonate (possible norsethite). This leads to the interpretation that penetrating fluids were Ba<sup>2+</sup>-bearing during reaction (2) preventing formation of magnesite by substituting Mg<sup>2+</sup> by Ba<sup>2+</sup>. There are a few MSI where the assemblage resulting from (2) is observed (see appendix 11.4 – A1). These can be formed in the absence of Ba<sup>2+</sup> during the prograde reaction.

Spinel grains in MSI have varying Cr#=58-91 (figure 19D) and show an overall relative enrichment in Cr compared to Al. The composition of spinel grains in MSI shows lower Al<sub>2</sub>O<sub>3</sub> oxide wt.% (average of 12.32 wt.%) than the M2 and M3A spinel grains and M3B-C spinel grains that do not come from MSI (total average at 26.99 wt.%) while the  $Cr_2O_3$  oxide wt.% of all spinel grains is in the same range (average of 45.29 wt.% for spinel in MSI against an average of 41.74 wt.% for the M2 and M3A spinel grains and M3B-C spinel grains that do not come from MSI).

Monazite is the depository mineral for LREE in the MSI and is often found as small grains (<1  $\mu$ m) in MSI (figure 30B). Because of the small size of monazite grains (largest grain ~2  $\mu$ m; see appendix 11.4 - A4) it is not possible to make age constraints using U-Pb of monazite and thus it was not possible to accurately determine the timing of monazite formation. The occurrence of monazite in MSI indicates that LREE's and P where mobile elements during fluid penetration. Cl-apatite indicates the same mobility for P and an additional presence of Cl in the penetrating fluids since these minerals are present in the same MSI (figure 30B).





Figure 30A-D. BSE images of common inclusions in orthopyroxene from location 4-18 (see appendix A2), oriented in the same direction. A) location 4-18-2: cpx + mgs + phl + apa + sp + C + a SiO<sub>2</sub>-phase, interpreted here as coesite. B) location 4-18-3: cpx + phl + BaMg-carbonate + apa +mnz + Aloxide, possible remnant of the Al<sub>2</sub>O<sub>3</sub> polishing agent. C) location 4-18-4: cpx + C + Fe,Cu sulphide. D) location 4-18-8: cpx + dol + apa (also see appendix 11.2 – location 4-18).

(calcite/dolomite/magnesite/BaMg-carbonate) + carbon + spinel (Cr#= 58-91) + Tiphlogopite + Cl-apatite ± monazite ± rutile ± (Fe,Ni,Cu) sulfide. Combinations of thesemineral phases in orthopyroxene MSI can be seen in figure 30A-D. In this figure itbecomes evident that the frequency of the minerals in MSI is not comparable to the vol.%in MSI. Clinopyroxene (diopside) for instance occupies a large volume in MSI and also Clapatite is usually present as a relatively large grain. The high frequency of carbon andcarbonate phases indicates that a C-saturated fluid penetrated the Bardane websterite. Itis unsure if the Fe-sulfide grain in figure 30C is part of the original MSI assemblage as it islocated at the edge of the inclusion along a crack in the orthopyroxene crystal. Asdiscussed above this individual grain could have been deposited during the exhumationevent.

Van Roermund et al. (2002) euhedral shaped reported carbon inclusions which growth. indicated diamond Occasionally some carbon phases in MSI in this study also occur as euhedral shaped crystals in orthopyroxene (figure 32 D-E; figure 33). Some carbon phases in clinopyroxene show a similar euhedral shape (figure 34). An attempt was also made to confirm if these carbon phases are diamonds by using Cathode



Figure 31. A) Raman spectrum of microdiamonds found by van Roermund et al. (2002). B) Raman spectrum of euhedral carbon inclusion at location 4-18-4 which shows an extra peak around 1580 (cm<sup>-1</sup>), which is indicative for graphite (Xu et al., 2003).



Figure 32. Multiphase solid inclusions in orthopyroxene from thin section 5. A) Thin section 5 in cross polarized light. B) Thin section 5 in plane polarizes light, red box is location 5-10. C) Plane polarized light image of location 5-10 showing elongated near horizontal inclusions in M2 orthopyroxene. D) BSE image of MSI in orthopyroxene containing cpx, phl, rt, mnz, sp, a carbon silicate (SiC, possible moissanite, FEG SEM XL-30 EDS spectrum is given) and a BaMg-carbonate. E) SE image of the Electron Microprobe showing distinct angles in the euhedral carbon inclusion (black mineral).

Luminescence on the Electron Microprobe. Van Roermund et al. (2002) used this method also to confirm if the carbon polymorphs were diamonds or graphite. Unfortunately this method did not give the confirmation that the carbon inclusions in this study are diamonds, there was no illumination at all. The recently arrived Raman spectrometer at the University of Utrecht (dr. H. King) provided another method to give confirmation that these euhedrally shaped crystals are not the carbon polymorph diamond, but graphite (see figure 31). But based on the euhedral shape of these particular inclusions it is reasonable to



Figure 34. Multiphase solid inclusions in M2 clinopyroxene from thin section 6. A) thin section 6 in cross polarized light. B) thin section 6 in plane polarizes light. C) plane polarized light image of location 6-20-11. D) BSE image (FEG SEM XL-30) of MSI in clinopyroxene containing phl(bio), (Cl-bearing) ap, tlc and carbon. E) SE image (Electron Microprobe) showing distinct angles in the carbon inclusion on the right from D).

believe that these carbon phases were once diamonds during at least the peak M3 stage and graphitized during exhumation. Actual presence of diamond would provide evidence for the minimal pressure at which the MSI have developed, since diamond occurrence would indicate UHP conditions (above 3.8 GPa). But there are other pressure indicators present in the multiphase solid inclusion assemblages. Figure 32D shows two FEG SEM XL-30 EDS spectra where a high C and Si peak is measured in a mineral adjacent to the euhedral carbon phase. Moissanite (SiC) is a mineral which fits the chemistry and pressure conditions (peak M3 is 6.34 GPa). HP-HT experiments have shown that natural moissanite forms at conditions of at least 6 GPa, 1430-1500 °C and extremely low  $fO_2$  which is at least five to six log units below Iron–Wüstite (IW) (Pierrol et al., 2003; Liang et al., 2014).



Figure 35. Two typical locations for multiphase solid inclusion in M2 orthopyroxene. A) orthopyroxene crystal cut perpendicular from thin section 4, location 13, showing clinopyroxene exsolution lamellae which are slightly brighter coloured (a few pointed out by arrows). B) orthopyroxene crystal cut parallel from thin section 5, location 10, showing near horizontal multiphase solid inclusion assemblages (a few pointed out by arrows).



Figure 36. A-C) Location 4-18 showing many MSI in M2 orthopyroxene. Figure D is the red box in figure C. Figures D and E are on roughly the same scale and show the difference between a view through the optical microscope (D) and a view by BSE (E) of the same MSI. Arrows in D and E point out the same MSI assemblage.

Figures 35 and 36 show more typical MSI in orthopyroxene, visible through the optical microscope and on FEG SEM XL-30 BSE images. Figures 36D-E nicely illustrate the difference in MSI viewed through the optical microscope or viewed by BSE. Appendix 11.4 - A1 shows some MSI assemblages in orthopyroxene where carbon phases clearly do not have an euhedral shape. Figure 34D shows this as well, a single euhedral carbon inclusion is less than 15  $\mu$ m away from a lenticular carbon inclusion which has no distinct angular shape. So apparently these two carbon phases can coexist in the same host mineral, but might have formed under different conditions. Interesting is that the only euhedral shaped carbon inclusion found in clinopyroxene (figure 34E) is not found being a part of a MSI. Whereas those found in orthopyroxene (figures 32E and 33) always form part of a MSI assemblage.

Figure 37 shows a histogram of the frequency vs type of solid inclusion in MSI in clinopyroxene. This figure does not show the different assemblages, but it gives an idea of the frequency of minerals in MSI common in clinopyroxene. Orthopyroxene and spinel are common minerals as slightly in well as, lesser occurrence, carbon, Cl-apatite, phlogopite and (Fe,Ni,Cu) sulfides. Talc and dolomite are not common and dolomite is found only once. This is a big difference with MSI in orthopyroxene where carbonates are common in inclusions. And monazite and rutile are found in MSI in orthopyroxene, but appear absent in MSI to be in clinopyroxene. A very common assemblage mineral in clinopyroxene is the combination of orthopyroxene and spinel (figure 38). So a Mg and Cr rich fluid has percolated though the rock enriching it in these elements and depleting it in Ca, following Mg + Cr + clinopyroxene = Ca +orthopyroxene + spinel. The absence of carbonates, monazite, and rutile suggests that the formation of MSI in clinopyroxene occurred at a possible different time, but with at least a different compositional fluid than during formation of MSI in orthopyroxene. Fluids rich in Mg, Cr and C are the main penetrating fluids in clinopyroxene during formation of MSI. Wang et al. (2016) interpreted Cr previously replenishment in depleted peridotites in parts of altered oceanic crust due to

reducing conditions. Reducing environments can cause fluids with mobile, oxidized, isotopically heavy Cr(VI) to experience partial reduction, which depleted the fluids and enriched peridotites in



Figure 37. Histogram showing the frequence (not vol. %) of all MSI in clinopyroxene. The bars do not represent volume percentage of minerals. Orthopyroxene and spinel are most frequently found, carbon, apatite, phlogopite and (Fe,Ni,Cu) sulphides are also common. Notable is that only one carbonate inclusion is found in clinopyroxene and no rutile and monazite.



Figure 38. BSE image of common inclusions in clinopyroxene: orthopyroxene + spinel. The dark grey spots are orthopyroxene inclusions, the bright dots are spinel inclusions, inside a clinopyroxene host mineral (light grey), from location 3-17.

heavy Cr(VI). The garnet websterite from Bardane and the surrounding peridotite lens could have experienced penetration by a fluid rich in isotopically heavy Cr(VI) which deposited assemblages of spinel and orthopyroxene in the clinopyroxene minerals under reducing conditions. The wt.%  $Cr_2O_3$  of spinel (i.e. mass fraction) in MSI in clinopyroxene is 34.66-39.67 and for the spinel in MSI in orthopyroxene this is 39.99-51.73 wt.%  $Cr_2O_3$ . So the absolute amount of Cr is higher in MSI in orthopyroxene than in MSI in clinopyroxene (see appendix 11.1 - T2 for wt. % oxides of elements in spinel in MSI). The difference in absolute  $Cr_2O_3$  wt.% can be the result of different valencies states of Cr during mobility under potentially different reducing conditions.

The dominant phases present in MSI in clinopyroxene are orthopyroxene + spinel  $\pm$  carbon  $\pm$  Cl-apatite  $\pm$  phlogopite  $\pm$  (Fe,Ni,Cu) sulfides  $\pm$  talc  $\pm$  dolomite. Where orthopyroxene and spinel are common in inclusions and combinations of carbon, phlogopite and Cl-apatite occur frequently. The (Fe,Ni,Cu) sulfides are present as small grains (low vol. %) and talc and carbonate are rare phases in MSI. The mobile elements in the pervasive fluid in clinopyroxene are Mg, Cr, C, P, Cl, minor K & Ti, and a minor amount of Ni, Fe, Cu & S. No LREE (e.g. monazite) are found in MSI in clinopyroxene, but this does not have to mean that these elements were absent in the pervasive fluids in clinopyroxene. LREE can be built in in clinopyroxene and not in orthopyroxene. That can be the reason that monazite is found in orthopyroxene MSI assemblages and not in clinopyroxene MSI assemblages.

The strong pressure vessels in which diamond-bearing MSI were included in M3A spinel grains, in turn enclosed in M3 garnet grains (van Roermund et al., 2002) are also present in the garnet websterite observed in this study. However MSI in spinels were not abundant



Figure 39. BSE images of MSI in spinel from location 6-13. A) Light grey spinel enclosed in garnet grain where inclusions are found. A symplectite is found at the spinel/garnet interface. B) The figure is the location of the red square in A. The red square in B points out the location of C. C) Enlargement of the MSI assemblage. D) EDS spectra and element occurrences in the different inclusions. Good measurements were difficult because of the small sizes of the inclusions. Apatite is present in the MSI, but notable is that this is without Cl which is varianting from the Cl-bearing apatite in MSI in clino- and orthopyroxene. The bright inclusion, visible in the central part of the MSI in C, is possible monazite. No LREE are detected, but a small P peak and the bright color are consistent with the signature for the mineral monazite (not apatite). Clino- and orthopyroxene inclusions are both present as are inclusions with a high Al and O peak, Al-oxides, on EDS spectra. It should be considered that the polishing agent for the thin sections is  $Al_2O_3$  and that the Al-oxides in the MSI might have been derived from this agent.

and only one good example is found during this study (figure 39). This MSI in spinel (Cr#=55) contains no carbon inclusions, but clinopyroxene, orthopyroxene, apatite (without Cl), possible monazite and a variable amount of Al-oxides are present. The element K is also detected which indicates possible presence of phlogopite in the inclusions. But most of the inclusions are so small (most inclusions are <1 $\mu$ m) that identification of minerals with EDS spectra is difficult and some interpretations are made by occurrence of elements in EDS spectra and brightness on the BSE image. The apatite inclusion stands out by the absence of Cl (see appendix 11.4 - A5 for EDS spectrum), this is in complete contrast to apatite inclusions in clino- and orthopyroxene which are all Cl-bearing apatite. The large amount of Al-oxide inclusions is also peculiar, Al-oxide is found in orthopyroxene in small cracks or deficiencies on the surface of the orthopyroxene mineral. But the surface in this spinel mineral appears to be smooth which indicates that the Al-oxide occurrence is not the result of Al<sub>2</sub>O<sub>3</sub> polishing agent left behind in cracks of deficiencies but might actually be an Al-oxide inclusion precipitated from subduction zone fluids.

Sulfide inclusions are found throughout the websterite, they appear in inclusions as well as in serpentine veins or inside cracks in garnet (figure 40). The sulfide grains contain a variety of elements (e.g. Fe,Ni,Cu) and combinations of them are found with exception of the combination Ni and Cu. Figure 40D shows such a grain present in a serpentine vein with zoned Fe, Ni and Cu concentrations (see appendix 11.2 for detailed map). Figure 40B shows Fe,Ni sulfide 'tails' in the central part of a small serpentine vein. These 'tails' originate in the larger Fe,Ni sulfide grains and eventually pinch out. This indicates mobility of sulfides during the formation of the serpentine veins. Since the sulfides are part of the original assemblage (Brueckner et al., 2002; van Roermund et al., 2002) and occur in inclusions and in the serpentine veins it is acceptable that the sulfide phase has been mobile throughout all stages of the websterite. Sulfides and subduction zone fluids don not mix due to the reducing environment and sulfur will only bind to the transition metals Fe, Ni and Cu available in the websterite here. Any combination of S or Ni and Cu with other elements, or incorporated as element in other minerals, are not found in the MSI, besides Fe which does participate in other mineral structures (e.g. spinel, garnet).





Figure 40. BSE images of the different phases of sulfides present in the garnet websterite A) A Cu sulfide vein inside a crack in garnet, location 5-12 B) Fe,Ni sulfides grown together with spinel and in the central part of a serpentine vein inside an olivine grain. This implies mobility of Fe,Ni sulfide during the formation of the serpentine veins, location 4-8 C) Several sulfides in serpentine, location 4-9 D) A cluster of (Fe,Ni,Cu) sulfides inside а late serpentine vein.

LREE (contained in monazite) are not found in MSI together with assemblages rich in Cr (e.g. spinel). LREE are found only twice with small amounts of Cr contained in phlogopite. A similar observation is made for Ba (contained in BaMg-carbonate) and LREE which are not found in combination with sulfide assemblages. So LREE preferentially do not occur together with minerals containing high amounts of Cr and are not found together with (Fe,Ni,Cu) sulfides. Ba is also not found in this study in combination with (Fe,Ni,Cu) sulfides. However the fact that Ba and LREE are not observed together with sulfides does not mean that this combination cannot occur together in MSI. The sulfide phase is a phase which does not mix with subduction zone fluids but is simply present in minerals formed throughout the existence of the rock as mentioned before. So it is likely that Ba and LREE occur together with sulfide phases in MSI although they are not observed in this study.

#### 7. Discussion

## 7.1 Oxygen fugacity

Tumiati et al. (2015) established different  $fO_2$  values for different bulk rock compositions and phase assemblages in a subducting oceanic crust under HP, with a relatively continuous distribution of  $\mathsf{O}_2,$  suggesting redox heterogeneity in subduction zones. The Bardane websterites have a fO<sub>2</sub> of -2-0 log units below  $\Delta$ FMQ while surrounding eclogite facies marbles from the Lindas Nappe have a  $fO_2$  of 2.5-3.0 log units above  $\Delta FMQ$  (Malaspina and Tumiati, 2012; Boundy et al., 2002). This suggest similar heterogeneity in fO<sub>2</sub> during the Scandian subduction cycle (figure 41). There is about 140 km lateral distance perpendicular to the orogenic range between the Lindas Nappe and Fjørtoft. So these locations have not been metasomatised under the same conditions, but the different  $fO_2$  values indicate that there are different reducing conditions in the same subduction zone. This might also be a factor to consider on a smaller scale where reducing conditions may change over the meter scale instead of kilometer scale, because the peridotite lens is only tens of meters wide and different bulk rock compositions are present in a small area. Evidence for this can lie in the assemblages of the MSI which could then show differences between each other. MSI in orthopyroxene show no significant differences between assemblages, MSI in clinopyroxene do not as well. But MSI in clino- and orthopyroxene have different common assemblages which can be indicative for changing conditions during metasomatism, or different stages of activity of metasomatism. The MSI assemblage in spinel MSI is in turn different than those from clino- and orthopyroxene.

## 7.2 Multiphase solid inclusion assemblages

Observed assemblages of MSI obtained in this study are all presented above, but it must be noted that only the surface is observed for MSI by using the BSE method and there might be more minerals present in MSI than is observed in this study by being not visible on the mineral surface. With this in mind it can be assumed that minerals found in the same host mineral are able to form MSI in any assemblage. COH-fluids are fluids where hydrous minerals are coexisting with carbonates, for the Bardane websterite, these are phlogopite and calcite/dolomite/magnesite/norsethite respectively. The fluids are derived by dehydration and decarbonation reactions in the subducting slab, containing the continental gneisses. The websterite is metasomatised by phases enriched in incompatible elements where the COH-fluids consists out of  $H_2O-CO_2$  mixtures (see figure 42) (Malaspina and Tumiati, 2012). The coexistence of carbonates, hydrous minerals and elemental carbon indicates that the oxidation state of the system has great influence on the fluid speciation (Malaspina et al., 2009). The dehydration processes in the subducting slab causes fluid flow to move through pervasive micro-fractures where MSI with different assemblages crystalize. The question is if dehydration and decarbonation processes occurred all at once, gradually or with pulses. High amounts of LILE are released when phengite completely breaks down in K-poor rock and this is the major source for LILE in subduction zone fluids. On the other hand K-rich rocks with a high amount of phengite and therefore no complete breakdown, will not enrich aqueous solutions in LILE and a continuous source of LILE is present (Zheng and Hermann, 2014). The presence of LILE's Ba and K in all MSI assemblages indicates a constant source for these elements and therefore the last scenario with a K-rich slab source rock is most likely.

Although there are different MSI assemblages between clino- and orthopyroxene the Csaturated supercritical fluid where they are derived from has contained the same elements based on the minerals present in MSI. This results in a fluid containing the derived elements which were not originally present in the rock: K, Na, Ti, P, Cl, Cr, (Fe, Ni, Cu), S and elemental C, and additional LREE (La and Ce) and Ba are found in orthopyroxene and



Figure 41. Conceptual model of Tumiati et al. (2015) illustrating oceanic subduction zone  $fO_2$  heterogeneity between the mantle wedge and the subducting slab, based on Mn-Fe metacherts (Praborna, Italy),  $nO_2$  is the molar quantity of  $O_2$ . An analogue with the Bardane websterites can be made which were equally positioned on the mantle wegde/slab interface during the Scandian subduction cycle. The subducting slab shows the stage M3A-C prograde sequence during subduction after Scambelluri et al. (2008) and van Roermund (2009).

Nb in rutile grains on the grain boundaries of phlogopite, while sulfides are interpreted to

be part of the M1 assemblage. Major trace element solutes Si, Al, Ca and Mg (and Fe already mentioned) are also mobile elements in the subduction zone fluid. These elements were originally present in the websterite lens in the main M3A minerals clino-, orthopyroxene, garnet and olivine and the subduction zone fluid could have derived these elements from the subducting slab or from the minerals already in place.

Hermann et al. (2013) suggested that Nb (and Y and Zr) are not recycled from the subducting slab, but are taken deeper into the mantle by subduction. This would mean that Nb, which is found in rutile grains in the garnet websterite, is not derived from subduction zone fluids, but is obtained from another source. Xiao et al. (2006) concluded in their study on hydrous rutile-bearing eclogitic layers from the Dabie-Sulu region that (the HFSE) Ti, Ta and Nb are mobile elements because of variable Nb/Ta ratios and the presence of thick rutile layers. Nb and Ta are immobile elements in the presence of rutile and therefore during mobility of Nb it can be assumed that rutile is not present. So if Nb is part of the subduction zone fluids than this would have been with concurrent mobility of Ti and in the absence of rutile grains. It has been observed that Ti is a mobile element in continental subduction zones, for instance in the Dabie-Sulu region, where combined



fluid where the  $fO_2$  for the Bardane websterite shows that the fluids consists out of a mixture of  $CO_2$  and  $H_2O$  (after Malaspina and Tumiati, 2012).

with the low solubility of HFSE in aqueous solutions it can be suggested that these elements can be transported over at least short distances by dissolution-reprecipitation reactions (Zheng and Hermann, 2014 and references therein). Mobility of Nb (and Ta) results from the breakdown of hydrous minerals like phengite and biotite and because of the detection of Nb, but no detection of Ta in rutile, Nb is preferentially incorporated into rutile. It is likely that Nb was recycled from the subducting slab in the WGR contrary to what Hermann et al., (2013) suggested.

MSI in spinel stand out because of the absence of Cl in apatite inclusions while this element is present in all other apatite minerals in MSI in clino- and orthopyroxene. What is observed in the EDS spectrum is a high oxygen peak which cannot be solely explained by measuring spinel as background value (figure 43). The oxygen peak for spinel is twice the height of the aluminum peak, an oxygen peak with a roughly equal height as the phosphor peak remains if this subtraction is done. If this is compared to the oxygen peak of a Clbearing apatite mineral in a MSI in orthopyroxene than it becomes clear that this is only half the height of the phosphor peak which is significantly lower than apatite in spinel. So Cl-bearing apatite is formed in MSI in clino- and orthopyroxene, but the hydrous OHbearing apatite is formed in MSI in spinel. Multiple Al-oxides are also found in this set of inclusions. As discussed earlier this is not believed to be thin section polishing agent because of the smooth surface of the spinel grains and the absence of cracks and deficiencies on the surface. This would indicate that an Al-rich fluid is responsible for these Al-oxide inclusions. The composition of the subduction zone fluid responsible for the MSI in spinel would then consist out of the elements: P, Al, K, Ca and OH. This is a different composition than the one derived for clino- and pyroxene MSI, but as discussed in the results there is only one set of inclusions found in spinel grains. This might not be enough to make interpretations of a possible different subduction zone fluid percolating through spinel and respectively clino- and orthopyroxene. Notable is the different apatite endmember and the high amount of Al-oxide in MSI in spinel. But due to the absence of observed inclusions in garnet this can be an isolated inclusion from a more aqueous fluid based on the presence of a hydroxyl apatite endmember.

The high Cr# of spinel grains in MSI compared to spinel grains formed in the M3B-C stage indicates a relative Cr-enrichment in the subduction zone fluids. The absolute values indicate a depletion of Al of 3.59-21.45 wt.% oxide to M3 Al content of 29.55-52.03 wt.% oxide. This explains the high Cr# of spinel grains in MSI, but indicates a fluid depleted in Al. while this is in sharp contrast to the Al-oxide inclusions found in the spinel host grain.



Figure 43. EDS spectra of apatite from the FEG SEM XL-30. A) Cl-bearing apatite  $Ca_5(PO_4)_3Cl$  in a MSI assemblage in orthopyroxene from location 4-19. B) OH-bearing apatite  $Ca_5(PO_4)_3OH$  with spinel background value from location 6-13.

Taken all observations into consideration and making the comparison to the derived composition of the subduction zone fluids responsible for the MSI in the garnet websterite studied by Carswell and van Roermund (2005) and the composition of the subduction zone fluid derived by this study, it can be said that these compositions are similar. Although kalsilite and zircon are minerals which are not found in this study nor is the element Th (and with zircon also Zr). It is very well possible that these elements are present in the garnet websterite from this study, but in such low concentrations that detection of them
has failed. Results on composition of the M2 clino-, orthopyroxene and garnet are very similar and differences of <1 wt.% oxide are measured. Summed up this gives two garnet websterites with the one in this study slightly richer in clinopyroxene, but with compositions of the main minerals within <1 wt.% oxide from each other and with the same determined mobile elements in the subduction zone fluid present in the MSI. Due to this great similarity between the two garnet websterites it is highly likely that the euhedral shaped elemental carbon inclusions found in the pyroxenes in this study were once microdiamonds, or graphitized microdiamonds.



Figure 44. Phase diagram from Malaspina and Tumiati (2012) showing C-O-H phase relations in metasomatised and K- and C-O-H-bearing peridotites and stability fields between carbonates and the prograde P-T path of the Bardane websterites shown as the green dots. The green dots represent the prograde sequence of the Scandian subduction cycle where M3-1 is the onset which is the equal stage as M3A in van Roermund (2009). Red dots are from peridotites of the Ulten zone, Italy.

## 7.3 Carbonates

The frequent occurrence of carbonates in the MSI can be compared to collected results by Malaspina and Tumiati (2012) on K- and C-O-H-bearing peridotites (figure 44). From this figure it can be seen that the only carbonate stable at pressures >3.1 GPa is magnesite. This is in contrast to the carbonate phases found in MSI in the Bardane garnet websterite. This is mostly dolomite and BaMg-carbonate (norsethite) and just a little occurrence of magnesite. But this is also observed by Scambelluri et al (2010) who found carbonate rods with dolomite cores replaced by magnesite. The same observations are made in this study (see appendix 11.2 – location 1-13), but still the majority of the carbonates are BaMg-carbonates which derived Ba from the subduction zone fluid and where Ba replaces Ca in dolomite. This will locate the formation pressure of the carbonates in the MSI above the

3.1 GPa and with the inferred occurrence of microdiamonds the assemblages of the MSI are consistent with the K- and COH-bearing peridotite stability phase diagram composed by Malaspina and Tumiati (2012).

Various carbonates are present in the MSI, calcite, dolomite, magnesite and a BaMgcarbonate. Semi quantitative spot analysis by the SEM XL-30 shows that amounts of Ba and Mg are equal and a candidate for this BaMg-carbonate is the earlier mentioned dolomite-analogue mineral norsethite  $[BaMg(CO_3)_2]$  (Pimentel and Pina, 2014). It should be noted that the experiments conducted by Pimentel and Pina (2014) were all at room temperature and at atmospheric pressure. Ba<sup>2+</sup> is a mobile element (LILE) in subduction zones and it can substitute for  $Ca^{2+}$  in dolomite  $[CaMg(CO_3)_2]$ . BaMg-carbonates in the MSI, with one exception, are always accompanied with the presence of clinopyroxene (diopside [MgCaSi<sub>2</sub>O<sub>6</sub>]). Scambelluri et al. (2010) observed carbonate inclusions with dolomite cores partly replaced by magnesite and surrounded by an outer thin rim of clinopyroxene against the orthopyroxene host shown in the reaction dolomite + orthopyroxene = magnesite + clinopyroxene (2). The observations in this study of BaMgcarbonates present together with clinopyroxene (diopside) lead to an incorporation of elemental  $Ba^{2+}$  in this reaction. A similar reaction can be written: dolomite + orthopyroxene +  $Ba^{2+} = BaMg$ -carbonate + clinopyroxene (3) occurring simultaneously as (2) depending on the availability of  $Ba^{2+}$  introduced as mobile element by the subducting slab. In figure 45 the stability fields of dolomite + orthopyroxene and magnesite + clinopyroxene are illustrated and at the onset of the Scandian orogeny (stage M3-1, indicated by the dark grey star) the microdiamond-bearing multiphase inclusions in Crspinel inside M3 corona garnet were formed (Van Roermund et al., 2002), as well as the carbonates mentioned in the reactions above, by COH-silicate fluids enriched in Ba<sup>2+</sup>. Both assemblages are found in MSI and therefore it is assumable that Ba<sup>2+</sup> enriched fluids have penetrated through some part the websterites, and in other parts of the websterite the  $Ba^{2+}$  enriched fluids have not percolated through or at least  $Ba^{2+}$  did not enter the

dolomite crystal structure, since there are no BaMg-carbonates, but only magnesite is present. Carbonate inclusions are common in M2 orthopyroxene megacrysts, rarely found but are in clinopyroxene. The carbon phase on the other hand is common in clinopyroxene as well as orthopyroxene. This can indicate that precipitation of carbonate was before crystallization of clinopyroxene. Or subduction fluids percolating through clinopyroxene were of reducing origin so carbonates were not able to precipitate in clinopyroxene, and carbonates in orthopyroxene are different from а fluid percolating event.

Observations show that almost all phases found in MSI are present in M2 orthopyroxene, whereas in the host minerals clinopyroxene and spinel not all phases have been found.



## 8. Conclusion

The MSI have precipitated from a pervasive subduction zone fluid which has an intermediate character between a hydrous melt and an aqueous fluid (i.e. supercritical fluid), which was enriched in LILE and LREE and slightly in HFSE. Mobile elements in the subduction zone fluids responsible for the precipitation of MSI in the Bardane garnet websterite are K, P, Cl, S, Na, Ti, Cr, Fe, Ni, Cu, elemental C and in lesser amounts LREE (La and Ce) and Nb. The major solute elements Ca, Mg, Si and Al are also part of this subduction zone fluid although these could have been derived from the host minerals

already present. The euhedral shape of the carbon inclusions in orthopyroxene and clinopyroxene is similar to euhedral shapes found in a similar garnet websterite from Bardane, together with the resemblance in element mobility confirmed by the similarity in MSI between the two different websterites, it is likely that these euhedral shapes are graphitized microdiamonds since Raman spectrometry confirmed these inclusions to be graphite. This result in turn proves that for the Bardan garnet websterite microdiamonds are only stable in the M3A spinel inside M3 garnet pressure vessels. Graphitized microdiamonds would be evidence for deep continental subduction (>130 km) in the Western Gneiss Region.

Although there is a slight apparent low occurrence of carbonates in MSI in clinopyroxene, compared to orthopyroxene, the elements and minerals present in the MSI in these two main minerals indicate precipitation of MSI from the same subduction zone fluid. MSI in spinel are different in the sense of a different apatite endmember which has a hydroxyl group bound to it instead of Cl. This can indicate an isolated inclusion in a M3A spinel where an aqueous Al-rich fluid is responsible for the precipitation of this particular MSI in spinel. Since there are no inclusions found in the surrounding garnet this is a possible scenario. Spinel grains in MSI have an overall high Cr# with an absolute lower oxide wt. % of Al compared to M2, M3A and M3B-C spinel grains, which means there is Cr mobility in subduction zone fluids. Higher absolute Cr wt. % oxide values of spinel in MSI in orthopyroxene compared to clinopyroxene indicates more Cr availability during precipitation of MSI in orthopyroxene.

ΔFMQ values for the Bardane websterite and the occurrence of relatively large elemental C crystals together with the abundance of carbon inclusion in the MSI assemblage indicates that a reducing environment was present during precipitation of the MSI. Occurrence of carbonates with carbon inclusions in the same assemblages indicates that not all carbonate is reduced to elemental C and oxygen fugacity might not have been constant throughout the penetration of the subduction zone fluids. Heterogeneity of the subducting slab at the slab-mantle interface, introducing different bulk rock compositions, can be the mechanism behind this.

Most inclusions contain silicate-rich phases like clino-, orthopyroxene and phlogopite. This indicates that also a silicate-rich fluids penetrated the Bardane garnet websterite, similar to conclusions of van Roermund et al (2002). Summing up all the components of the different MSI assemblages of the minerals, the subduction zone fluid was an immiscible C-saturated COH-, silicate- and sulfide-rich (supercritical) fluid. Where LILE, HFSE and LREE were released from the subducting slab by dehydration reactions forming fluids rich in solutes which were pervasive and precipitated minerals as MSI in the garnet websterite in a reducing environment.

Future research should focus on MSI assemblages in spinel. From this study it can be concluded that inferred microdiamonds are not stable in ortho- and clinopyroxene. Microdiamonds can be present in M3A spinel inside M3 garnet. A larger surface should be studied to search for microdiamond-bearing MSI assemblages in these spinel/garnet settings.

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11. Appendix – 11.1 Tables

Mineral phase Sample no.	M2 Cpx1 6-20-11	M2 Cpx2 6-20-11	M2 Cpx3 6-20-11	M2 Cpx avg. 6-20-11	Cpx-lam1 6-20-11	Cpx-lam2 6-20-11	Cpx-lam avg. 6-20-11
Anal. Method	EMP	EMP	EMP	EMP	EMP	EMP	EMP
Oxide wt. %							
SiO2	54,97	55,16	55,08	55,07	54,81	54,68	54,75
TiO2	0,04	0,08	0,11	0,08	0,06	0,08	0,07
AI2O3	3,14	4,07	3,80	3,67	3,35	3,29	3,32
FeO*	1,45	1,50	1,66	1,54	1,29	1,32	1,31
MnO	0,06	0,07	0,09	0,07	0,06	0,05	0,05
MgO	15,57	14,89	15,84	15,43	15,01	15,03	15,02
CaO	20,65	20,11	19,61	20,12	20,23	20,39	20,31
Na2O	2,41	2,84	2,58	2,61	2,66	2,58	2,62
NiO	0,00	0,04	0,01	0,02	0,02	0,03	0,02
Cr2O3	1,78	1,77	1,77	1,77	2,70	2,67	2,69
Total	100,07	100,53	100,55	100,38	100,19	100,12	100,15

T1. Electron Microprobe data of clinopyroxene

Mineral phase	spinel	spinel	spinel	spinel	spinel	spinel	spinel
Host mineral	орх	орх	срх	орх	срх	орх	орх
Sample no.	1-13-01	1-13-02	6-21	2-13-03	3-19-03	4-19-01	5-11-09
Anal. Method	EDS	EDS	EDS	EDS	EDS	EDS	EDS
Oxide wt. %							
SiO2	8,18	17,22	14,20	0,00	13,07	9,96	4,62
TiO2	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Al2O3	15,59	9,09	16,94	21,45	12,32	3,59	6,47
FeO*	17,56	16,61	12,33	14,27	17,63	21,18	21,46
MgO	14,54	17,09	21,87	14,84	17,31	13,54	7,51
Na2O	1,32	0,00	0,00	0,00	0,00	0,00	0,00
Cr2O3	42,81	39,99	34,66	49,44	39,67	51,73	51,46
C2O	0,00	0,00	0,00	0,00	0,00	0,00	8,48
Total	100,00	100,00	100,00	100,00	100,00	100,00	100,00

T2. EDS data of the FEG SEM XL-30 on spinel grains in MSI with different host minerals

	SEM	SEM	
anal. Method	XL-30	XL-30	EMP
sample no.	4-7	4-13	6-20-11
location	core	core	core
wt.% oxide			
SiO2	52,72	54,72	54,75
AI2O3	6,56	3,53	3,32
FeO	2,80	2,18	1,31
MgO	14,92	14,66	15,02
CaO	18,77	18,66	20,31
Na2O	2,28	2,90	2,62
Cr2O3	2,58	3,35	2,69
total	100,63	100,00	100,16

T3. EMP and SEM XL-30 data on cpx lamellae

	SEM	SEM	SEM	SEM	
anal. Method	XL-30	XL-30	XL-30	XL-30	EMP
sample no.	3-18	4-12	4-5	5-13	6-20-11
location	core	core	core	core	core
wt.% oxide					
SiO2	54,47	54,63	54,05	56,65	55,07
AI2O3	4,02	3,50	3,59	4,21	3,67
FeO	2,46	2,47	2,54	2,20	1,54
MgO	15,43	15,15	15,42	16,81	15,43
CaO	18,48	18,99	18,63	17,35	20,12
Na2O	3,10	2,48	3,04	2,77	2,61
Cr2O3	2,03	2,78	2,83		1,77
total	99,99	100,00	100,10	99,99	100,39
	1 20 4-1	M			

T4. EMP and SEM XL-30 data on M2 cpx  $% \left( {{\rm{T}}_{\rm{T}}} \right)$ 

anal. Method	SEM XL- 30	SEM XL- 30	SEM XL- 30	SEM XL- 30
sample no.	4-18-3	4-18-8	5-10-3	5-13-1
location	Inclusion	Inclusion	Inclusion	Inclusion
wt.% oxide				
SiO2	54,63	53,52	54,53	53,29
Al2O3	2,91	2,85	3,71	2,81
FeO	3,54	2,97	2,53	2,16
MgO	20,68	17,85	15,97	17,23
CaO	13,39	17,87	17,62	20,27
Na2O	2,15	2,13	2,64	2,10
Cr2O3	2,70	2,79	3,01	2,14
total T5. EMP and SEM >	100,00 L-30 data	99,98 a on cpx i	100,01 nside MSI	100,00

	SEM	SEM	SEM	SEM	SEM	SEM	SEM	
anal. Method	XL-30	XL-30	XL-30	XL-30	XL-30	XL-30	XL-30	EMP
sample no.	4-8	4-6	4-11	5-9	5-12	6-16	6-13	6-13
location	core	core	core	core	core	core	core	core
wt.% oxide								
SiO2	40,49	42,55	41,65	42,11	42,47	42,74	42,53	41,89
AI2O3	21,24	20,16	21,00	20,62	21,38	20,82	21,50	21,39
FeO*	9,53	8,52	7,74	8,82	7,02	7,89	8,15	7,89
MnO								0,43
MgO	19,49	18,79	20,19	18,97	20,28	20,39	19,68	20,75
CaO	5,00	5,32	4,51	5,16	5,18	4,65	4,55	4,65
Cr2O3	4,42	4,66	4,92	4,32	3,66	3,52	3,59	3,50
Total	100,17	100,00	100,01	100,00	99,99	100,01	100,00	100,59
Cr#	12,2	13,4	13,6	12,3	10,3	10,2	10,1	10

T6. EMP and SEM XL-30 data on garnet, including Cr#  $\,$ 

ar M sa	nal. ethod ample	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-3	SE 30 XL 6-2	M S -30 X 20-	EM L-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30
no	Э.	1-11	1-6	1-9	6-13	6-12	2 8	6	-8	2-19	2-19	2-20	2-20	3-12	3-12	3-13	3-08
lo w o>	cation t.% kide	core	core	core	core	core	CO	e co	ore	rim	core	rim	core	core	rim	core	core
Al	203	5,87	12,49	19,4	4 34,15	5 30	,64 25	,51	21,73	34,91	52,03	34,29	27,99	38,84	32,56	11,83	30,54
Fe	eO*	28,18	16,93	20,8	3 11,3	3 10	,03 1	3,4	11,63	16,22	10,57	14,18	16,35	12,22	11,61	26,39	18,38
Μ	gO	5,31	12,64	11,35	5 19,74	l 19	,85 17	,49	19,74	12,51	15,79	16,11	14,19	17,81	14,38	5,66	13,29
Cı	r203	60,64	57,96	48,45	5 34,8	39	,49 4	3,6	46,91	36,36	21,62	35,42	41,47	31,12	28,09	56,12	37,79
to	tal	100	100,02	100	) 99,99	9 100	,01	100 1	.00,01	100	100,01	100	100	99,99	86,64	100	100
Cı	r#	87,4	75,7	62,6	5 40,6	5 4	6,4 5	3,4	59,2	41,1	21,8	40,9	49,8	35,0	36,7	76,1	45,4
St	tage	M2	M2	-	M3A	M3A	. МЗ	A M	3A	МЗВ-С	МЗВ-С	M3A	МЗА	M3B-C	МЗВ-С	M2	M3A
	anal. Method sample	SEM 1 XL-3	SEM 30 XL-3	I SE 30 XL	EM S 30 X	EM L-30	SEM XL-30	SEM XL-3	SEN 0 XL-	4 SEM 30 XL-3	SEM 0 XL-30	SEM ) XL-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30
	no.	3-9	4-8	4-	10 4	-9	4-7	4-13	4-1	4 4-15	4-5	5-9	5-9	5-7-1	5-7-1	5-7-2	5-7-2
	location wt.% oxide	n core	core	e co	re c	ore	core	core	core	e core	core	core	rim	core	rim	core	rim
	AI2O3	43	.03 39	70 /			44.04							10.00	10.00	10 20	10.20
			,00 00	,/9 -	15,51	45,27	41,24	7,	15 10,	.91 6,1	.5 15,7	2 26,28	3 32,62	19,09	19,80	10,50	19,29
	FeO*	13	,18 15	,79 - ,97 1	.3,94	45,27 16,08	41,24	7, 27,	15 10, 03 22,	.91 6,1 .76 26,6	.5 15,7 59 17,8	2 26,28 1 16,92	3 32,62 2 15,54	19,09 14,35	19,80	14,06	19,29
	FeO* MgO	13 16	,18 15 ,81 16	,79 2 ,97 1 ,78 1	.3,94 .8,37	45,27 16,08 18,29	41,24 10,22 20,55	7, 27, 5,	15 10, 03 22, 36 7,	.91 6,1 .76 26,6 .68 6,8	.5 15,7 59 17,8 36 12,0	2 26,28 1 16,92 8 12,28	3 32,62 2 15,54 3 15,93	19,09 14,35 13,92	19,80 14,05 13,65	18,38 14,06 12,93	19,29 14,78 13,59
	FeO* MgO Cr2O3	13 16 26	,18 15 ,81 16 ,98 27	,79 2 ,97 1 ,78 1 ,46 2	.3,94 .8,37 22,18	45,27 16,08 18,29 20,36	41,24 10,22 20,55 27,98	7, 27, 5, 60,	15 10, 03 22, 36 7, 47 58,	.91 6,1 .76 26,6 .68 6,8 .65 60	.5 15,7 59 17,8 36 12,0 ,3 54,3	2 26,28 1 16,92 8 12,28 9 44,52	<ol> <li>32,62</li> <li>15,54</li> <li>15,93</li> <li>35,91</li> </ol>	19,09 14,35 13,92 52,65	19,80 14,05 13,65 52,51	14,06 12,93 54,62	19,29 14,78 13,59 52,34
	FeO* MgO Cr2O3 total	13 16 26	,18 15 ,81 16 ,98 27 100 1	,79 1 ,78 1 ,46 2	.3,94 .8,37 22,18 100	45,27 16,08 18,29 20,36 100	41,24 10,22 20,55 27,98 99,99	7, 27, 5, 60, 100,	15 10, 03 22, 36 7, 47 58, 01 1	.91 6,1 .76 26,6 .68 6,8 .65 60 .00 10	.5 15,7 59 17,8 36 12,0 ,3 54,3 00 10	2 26,28 1 16,92 8 12,28 9 44,52 0 100	<ul> <li>32,62</li> <li>15,54</li> <li>15,93</li> <li>35,91</li> <li>100</li> </ul>	19,09 14,35 13,92 52,65 100,01	19,80 14,05 13,65 52,51 100,01	14,06 12,93 54,62 99,99	14,78 13,59 52,34 100
	FeO* MgO Cr2O3 total Cr#	13 16 26 2	,18 15 ,81 16 ,98 27 100 1 .9,6 3	,79 1 ,78 1 ,46 2 100 1,6	.3,94 .8,37 .2,18 100 24,6	45,27 16,08 18,29 20,36 100 23,2	41,24 10,22 20,55 27,98 99,99 31,3	7, 27, 5, 60, 100, 85	15 10, 03 22, 36 7, 47 58, 01 1 5,0 78	91 6,1 ,76 26,6 ,68 6,8 ,65 60 ,00 10 8,3 86	.5 15,7 59 17,8 36 12,0 ,3 54,3 00 10 ,8 69,	2 26,28 1 16,92 8 12,28 9 44,52 0 100 9 53,2	<ol> <li>32,62</li> <li>15,54</li> <li>15,93</li> <li>35,91</li> <li>100</li> <li>42,5</li> </ol>	19,09 14,35 13,92 52,65 100,01 64,9	19,80 14,05 13,65 52,51 100,01 64,0	14,06 12,93 54,62 99,99 66,6	19,29 14,78 13,59 52,34 100 64,5

anal. Method	SEM XL-30	SEM XL-30	SEM XL-30	EMP	Average composition
sample no.	5-2	5-11	5-1	6-13	for spinel from different stages
location	core	core	core	core	
wt.% oxide					wt.% oxide
AI2O3	21,42	12,68	15,81	25,11	14,83 26,44 40,79
FeO*	16,09	20,03	17,25	15,02	18,68 14,20 13,14
MgO	14,04	12,09	11,42	13,73	11,00 16,24 17,27
Cr2O3	48,45	55,21	55,52	45,62	55,49 42,44 27,77
total	100	100,01	100	99,47	100,00 100,15 100,00
Cr#	60,3	74,5	70,2	64,0	71,79 52,04 31,53
Stage	M3A	M2	M2	M3A	M2 M3A M3B-C

T7. Analyses results on spinel grains.

	oxide wt	.%									
Point	SiO2	TiO2	Cr2O3	CaO	Al2O3	MgO	FeO	MnO	NiO	ZnO	Total
1	56,77	0,06	1,37	1,36	1,63	34,10	4,10	0,09	0,08	0,02	99,84
2	57,61	0,06	1,03	0,18	1,11	36,30	4,17	0,08	0,06	0,01	100,64
3	0,12	0,00	40,36	0,05	30,42	15,52	13,17	0,21	0,09	0,18	100,31
4	0,04	0,03	41,00	0,03	29,80	15,36	13,19	0,24	0,05	0,25	100,17
5	0,06	0,04	44,58	0,03	26,05	14,14	14,79	0,25	0,08	0,17	100,46
6	0,04	0,06	45,86	0,03	24,92	13,65	15,06	0,27	0,09	0,23	100,40
7	0,04	0,07	45,85	0,01	24,95	13,73	15,18	0,26	0,10	0,11	100,57
8	0,03	0,06	45,83	0,01	24,96	13,74	14,79	0,28	0,07	0,17	100,18
9	0,02	0,09	45,54	0,01	25,42	13,92	14,93	0,24	0,10	0,21	100,72
10	0,05	0,04	45,42	0,02	25,22	13,97	15,02	0,24	0,11	0,19	100,49
11	2,57	0,06	43,17	0,04	23,68	13,16	14,41	0,24	0,10	0,09	97 <i>,</i> 96
12	0,03	0,04	45,36	0,01	25,32	13,80	14,91	0,24	0,09	0,04	100,08
13	0,01	0,06	45,75	0,00	25,30	13,79	15,02	0,26	0,08	0,18	100,68
14	0,06	0,06	45,38	0,00	25,11	13,65	14,95	0,28	0,08	0,18	100,00
15	0,00	0,07	45,66	0,00	25,16	13,65	15,00	0,27	0,07	0,20	100,25
16	0,02	0,07	45,54	0,00	25,22	13,73	14,98	0,26	0,06	0,20	100,28
17	0,02	0,10	45,81	0,00	25,17	13,70	15,14	0,26	0,07	0,23	100,70
18	0,01	1,46	45,54	0,01	24,53	13,51	14,90	0,27	0,09	0,12	100,72
19	0,01	1,64	45,57	0,01	24,25	13,52	15,03	0,26	0,08	0,22	100,88
20	0,03	0,33	45,76	0,01	24,78	13,71	15,00	0,23	0,07	0,17	100,35
21	0,03	0,21	45,66	0,01	25,04	13,75	15,25	0,24	0,11	0,15	100,69
22	0,02	0,11	45,71	0,02	25,17	13,68	15,22	0,26	0,09	0,16	100,69
23	0,03	0,07	46,09	0,03	25,49	13,72	15,15	0,25	0,13	0,22	101,40
24	0,04	0,08	44,76	0,04	25,91	13,94	15,02	0,26	0,08	0,18	100,54
25	0,08	0,05	42,39	0,08	28,53	14,90	14,07	0,22	0,09	0,20	100,79
26	38,76	0,19	13,19	15,25	10,44	14,76	4,83	0,07	0,04	0,13	99,57

T8. Composition data of spinel linescan at location 6-13. See appendix A7 for location of linescan.

anal. Method	SEM XL-30	EMP							
sample no.	6-20-11	1-11	3-13	3-11	3-8	4-10	4-13	4-15	4-15
location	core	core							
wt.% oxide									
SiO2	46,24	25,83	31,37	43,30	41,81	44,60	41,14	39,96	41,05
TiO2	2,06	3,86	6,03	6,83	6,29	2,11	7,14	6,31	5,58
AI2O3	17,02	11,41	11,49	17,48	16,03	16,91	14,93	15,43	14,51
FeO*	1,73	5,46	2,71	-	2,83	2,69	3,71	3,77	2,71
MgO	25,42	17,11	16,68	22,87	23,49	25,05	22,28	21,54	22,16
K2O	7,53	4,95	6,96	9,52	9,55	0,92	8,69	9,42	10,44
Cr2O3	-	10,29	1,78	-	-	2,13	2,10	3,56	2,63
total	100,00	100,00	99,99	100,00	100,00	100,00	99,99	99,99	99,43
Mg#	93,6	75,8	86,0	-	89,2	90,3	85,7	85,1	89,1

anal. Method	SEM XL-30	SEM XL-30	SEM XL-30	SEM XL-30
sample no.	2-20	4-18-3	4-19	5-13
location	MSI	MSI	MSI	MSI
wt.% oxide				
SiO2	41,16	49,39	42,97	41,07
TiO2	2,02	3,23	13,93	13,26
AI2O3	17,88	8,67	-	12,36
FeO*	2,35	3,38	4,14	4,64
MgO	25,05	27,41	25,64	20,45
K2O	9,12	5,56	7,21	2,75
Cr2O3	2,41	2,37	6,12	4,62
total	99,99	100,01	100,01	99,15
Mg#	91,4	89,0	86,1	81,5

T9. Compositional data of phlogopite present as grain or as part of MSI assemblage, for location 3-11 no FeO<sup>tot</sup> was measured and therefore Mg# could not be calculated.

anal. Method	EMP	EMP
sample no.	4-13-1	4-13-2
location	core	core
wt.% oxide		
Nb2O3	1,5:	1 2,01
TiO2	98,4	5 97,99
Total	100	0 100

T10. Analyses of rutile grains.



11.2 Appendix – Thin sections and study locations – BSE images

Polarized light image of thin section 1, red squares refer to study locations, shown in more detail with BSE images below.







Polarized light image of thin section 2, red squares refer to study locations, shown in more detail with BSE images below.













Polarized light image of thin section 4, red squares refer to study locations, shown in more detail with BSE images below.







A8. Map export of elements Mg, Cu, S, Ni and Fe of a zoned (Fe, Ni, Cu) sulphide inclusion in a serpentine vein.





BSE image of location 4-13, purple dots show analysis locations, the two purple dots, numbered one and 2, in the rutile grains correspond with the EMP analyses locations from Appendix 11.1 - T10.



BSE image of location 4-15, purple dots show analysis locations, EMP measurement location is indicated.









Polarized light image of thin section 5, red squares refer to study locations, shown in more detail with BSE images below.











Polarized light image of thin section 6, red squares refer to study locations, shown in more detail with BSE images below.



BSE image of location 6-13, purple dots show analysis locations, purple line show location of EMP linescan.







A2. BSE image of MSI in orthopyroxene, dolomite and magnesite are abundant phases here.




## Untitled:6







11.4 Appendix – Thin section sample locations from 62 Fjørtoft 1

62 Fjørtoft 1, showing the location of the studied inside the garnet websterite lens rock slice used in this study.



62 Fjørtoft 1 rock slice showing the thin section sampling locations. Numbers correspond with numbers for thin sections.