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Title: Highly depleted cratonic mantle in West Greenland extending into diamond stability field in the Proterozoic

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#### Abstract: Abstract

This study presents electron microprobe data for dunite xenoliths from a lamprophyre dyke located on the island of Qegertaa, West Greenland. The minimum age of this dyke is Palaeoproterozoic and it experienced amphibolite facies metamorphism and deformation during that era. The samples consist of nearly 200 xenoliths with a size range of 0.5-8 cm. These dunite xenoliths have olivine Mg#, that range from 80.3 to 94.6 (n = 579) with a mean of 92.6. Orthopyroxene is found in three xenoliths and garnet in five others. The latter suggests the depth of the Qegertaa xenolith suite to be near the diamond stability-field, which is substantiated by the finding of diamonds in bulk samples of the Qegertaa dyke. This further indicates the presence of a lithospheric mantle domain dominated by high-Mg# dunite to this depth in Palaeoproterozoic time. Cr-rich spinel, in the 0.1-0.2 mm size range, is found within and between olivine grains in individual xenoliths. These Cr-spinels yield Fe-Mg exchange temperatures of 400-600°C. However, the presence of intermediate spinel compositions spanning the lower temperature solvus suggests that equilibration temperatures were >550°C. Fe3+#, expressed as 100xFe3+/(Fe3++Al+Cr)), is shown to be a useful parameter in order to screen for altered spinel (Fe3+#>10) with disturbed Mg# and Cr#. The screened spinel data (Fe3+#<10) show a distinctly different trend in terms of spinel Cr# versus Mg#, compared to unmetamorphosed xenoliths in Tertiary lavas and dikes from Ubekendt Ejland and Wiedemann Fjord, respectively, also located within the North Atlantic craton. This difference likely reflects amphibolite facies metamorphic resetting of the Qegertaa xenolith suite by Fe-Mg exchange. Given the similarity of the Qegertaa xenolith suite with the Ubekendt and Wiedemann suites, in terms of their olivine Mg# and spinel Cr# distribution, high-Mg# dunite is likely to be an important component of the subcontinental lithospheric mantle beneath the North Atlantic craton and appears to have spanned a vertical distance of at least 150 km in this region, even during the Palaeoproterozoic.

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- We present EMP data for a new suite of dunite xenoliths from a lamprophyre dyke in West Greenland.
- Olivine Mg# averages 92.6 and garnet is present together with macrodiamonds.
- Spinel Cr# for this suite appears overprinted by metamorphism and formation of mica coatings.

# Highly depleted cratonic mantle in West Greenland extending into diamond stability field in the Proterozoic Stefan Bernstein<sup>a</sup>, Kristoffer Szilas<sup>b,\*</sup>, Peter B. Kelemen<sup>b</sup> <sup>a</sup> Avannaa Resources, Dronningens Tværgade 48 st.tv, 1302 Copenhagen K, DK <sup>b</sup> Lamont-Doherty Earth Observatory, PO Box 1000, Palisades, NY 10964-8000, USA <sup>c</sup> Corresponding author. E-mail: kszilas@ldeo.columbia.edu (K. Szilas)

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26 Cr# versus Mg#, compared to unmetamorphosed xenoliths in Tertiary lavas and dikes from 27 Ubekendt Ejland and Wiedemann Fjord, respectively, also located within the North Atlantic craton. 28 This difference likely reflects amphibolite facies metamorphic resetting of the Qegertaa xenolith 29 suite by Fe-Mg exchange. Given the similarity of the Qeqertaa xenolith suite with the Ubekendt and 30 Wiedemann suites, in terms of their olivine Mg# and spinel Cr# distribution, high-Mg# dunite is 31 likely to be an important component of the subcontinental lithospheric mantle beneath the North 32 Atlantic craton and appears to have spanned a vertical distance of at least 150 km in this region, 33 even during the Palaeoproterozoic.

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# 37 1. Introduction

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39 Determining the composition of the subcontinental lithospheric mantle (SCLM) has implications for 40 our understanding of the crust-mantle system and its evolution through time. Previous studies on 41 SCLM xenoliths from Greenland have shown the occurrence of nearly monomineralic dunites consisting of remarkably refractory olivine with molar Mg/(Mg+Fe<sup>2+</sup>), or Mg#, averaging about 42 43 92.8 (e.g. Bernstein et al., 1998, 2006, Bizzarro and Stevenson, 2003; Garrit, 2000; Wittig et al., 44 2008). The Qegertaa xenolith suite presented in this study shows equally refractory olivine 45 compositions. This growing body of data on cratonic mantle xenoliths from Greenland suggests that 46 such olivine-rich mantle is common here, and perhaps comprises a large proportion of the 47 lithospheric mantle beneath substantial parts of Greenland.

High and consistent Mg# in olivine is thought to reflect partial melting of the mantle to the point
of exhaustion of orthopyroxene (Bernstein et al., 2007). The implied high degree of melting (3745%; Bernstein, 1998; Herzberg, 2004) is not achieved in any current geological environment and
is thus thought to reflect a hotter mantle during the formation of cratonic SCLM. This is in

52 agreement with the generally Archaean Re-depletion ages of cratonic SCLM xenoliths (e.g. Hanghøj et al., 2001; Pearson et al., 2003; Shirey and Walker, 1998; Wittig, 2010) and the inferred 53 hotter mantle at that time (Herzberg et al., 2010). However, the exact formation environment is still 54 55 debated with one model proposing a single-stage process in a polybaric melting column either in a 56 spreading ridge or plume environment (e.g. Aulbach et al., 2011; Bernstein et al., 1998, 2006; Griffin et al., 2009; Herzberg et al., 2010; Kelemen et al. 1998), whereas another model proposes 57 58 flux melting of previously depleted harzburgite in a subduction zone setting (e.g. Canil, 2004; Lee, 59 2006; Wittig et al., 2008).

60 In addition to documenting the composition of the Palaeoproterozoic xenolith suite at Qegertaa 61 this study also shows that although parameters such as Mg#, and molar Cr/(Cr+Al), or Cr#, may at first appear to retain information of the primary composition of a mantle xenolith suite, examination 62 of molar  $Fe^{3+}/(Cr+Al+Fe^{3+})$ , or  $Fe^{3+}$ , in associated spinels reveals a history of alteration that 63 64 strongly modified both Mg# and Cr# so that even visually unaltered spinel had its chemistry overprinted during amphibolite facies metamorphism. Thus, spinel compositions, which are widely 65 66 thought to be reliable indicators of primary igneous conditions in metamorphic intrusive rocks (e.g. 67 Barnes, 2000) may reflect re-equilibration during metamorphic events (Evans and Frost, 1975; Sack 68 and Ghiorso 1991).

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### 70 2. Geology

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The Qeqertaa xenolith suite is hosted by an up to 6 m wide vertical dyke of ultramafic lamprophyric affinity, which crops out on the small island Qeqertaa, some 50 km north of Ilulissat at 69°38N, 50°38W (Fig. 1). The dyke is one of many that cut late Archaean gneisses and supracrustal rocks in the Ataa area, eastern Disko Bay (Garde and Steenfelt, 1999; Larsen and Rex, 1992; Marker and Knudsen, 1989). The Qeqertaa dyke has not been dated, but similar intrusions in the Ataa area have yielded K-Ar ages of 1782 Ma and 1743 Ma, both ±70 Ma (Larsen and Rex, 1992). Because the dykes have been affected both by metamorphism and deformation linked to the Palaeoproterozoic Rinkian-Nagsoqtuqidian orogeny, these ages could represent metamorphic overprinting and thus represent minimum ages, as pointed out by Larsen and Rex (1992). Structural interpretation suggests that the Ataa region can be divided into a series of crustal blocks with distinct tectono-magmatic history (Garde and Steenfelt, 1999) and the Qeqertaa dyke is situated in the border zone between the Ataa domain to the north and the Rodebay domain to the south.

84 The Qegertaa xenoliths are rounded to subangular, with a size range of 0.5 cm to 8 cm in the 85 longest dimension. In several places along the dyke, the xenoliths are so abundant as to make a 86 clast-supported network. The dyke has brecciated contacts with tonalitic gneisses, and is deformed 87 with pinch and swell structures. Apophyses are often sheared into tight isoclinal folds. Deformation 88 mainly affected the matrix, which often shows carbonate crystallization in pressure shadows of the 89 xenoliths and matrix foliation wrapping around individual xenoliths (Fig. 2). Matrix mineralogy is 90 dominated by tremolite, mica, carbonate, ilmenite and iron oxides. Of these minerals, only mica and 91 ilmenite are thought to remain from the primary mineralogy of the dyke matrix, although even these 92 minerals show evidence of alteration and recrystallization, manifested as oxide exsolution along 93 cleavage planes in mica, and exsolution lamellae and oxidized microcrystalline overgrowth zones 94 on ilmenite.

95 A collection of nearly 200 xenolith samples form the basis of this study. Individual xenoliths 96 larger than about 3 cm were cut into several slices 5-8 mm thick and all xenoliths were inspected 97 visually before a subset of 119 xenoliths of varying size were prepared for standard polished thin 98 sections and analysed by electron microprobe. The xenolith suite as a whole appeared very 99 homogeneous in terms of mineral mode, texture and grain size. The xenoliths are all dunites with 100 only a few samples containing spinel, garnet, mica or orthopyroxene (see below). A few xenoliths 101 are completely serpentinised, while others are relatively fresh peridotite with only local alteration 102 along minor cracks and veins. However, as shown below, all studied xenoliths have experienced 103 some degree of chemical modification of their primary minerals even though they at a first glance

appear nearly unaltered. Typically, in standard thin sections olivine grain margins are yellowish to light brown, in some samples more dusty brown (Figs. 2 and 3). Such margins can be relatively wide (1-2 mm), but are mostly in the order of 0.2-0.6 mm, such as in the example of xenolith sample qq-2 in Fig. 3. Spinel is often oxidized, with irregular grain margins and is opaque in standard thin sections. In rare cases, the spinel has retained a brownish translucent core. Secondary oxide, mainly magnetite, is common along veins and cracks within olivine grains and at the rim of individual xenoliths (Fig. 3). Some examples of xenoliths and their textures are given in Fig. 2a-d.

111 All xenoliths are coarse protogranular, following the terminology of Mercier and Nicolas (1975). 112 Grain size varies from 1-2 mm to >30 mm for olivine. Representative smaller xenoliths are 113 composed of only a few olivine grains. Well-rounded olivine megacrysts up to 30 mm are 114 frequently found in the matrix. An example of one coarse grained xenolith is given in Fig. 3, with 115 olivine grain size ranging 1-15 mm. Orthopyroxene, found in three xenoliths, occurs as  $\sim 1$  mm 116 wide circular inclusions in large olivine grains (Fig. 2). Garnet, found in five xenoliths (out of 200), 117 occurs as rounded 1-2 mm grains, but one 4 mm rounded garnet grain appears in xenolith #463737-118 1. Only one garnet is partly preserved (sample #463711), while all other grains have been 119 completely replaced by kelyphite (Fig. 2c). Cr-rich spinel is found as minute anhedral inclusions in 120 the 0.1-0.2 mm size range within olivine, or between olivine grains. Relic brown translucent spinel 121 is sometimes found, jacketed by opaque oxide, and nearly always with a thin (20-50 um wide) 122 coating of mica forming the outer contact to host olivine (Figs. 6a, 7a, 8a). Chrome-bearing 123 magnetite occurs throughout the xenoliths, as irregular larger grains (1-2 mm), possibly replacing 124 primary chrome spinel. It also occurs as smaller individual grains or aggregates of smaller grains 125 (0.1-0.3 mm), often associated with fractures or veins in olivine. These chrome bearing magnetite 126 grains likely represent alteration products. Primary mica is found in two xenoliths. In sample 127 #463707-2, a 2 mm long colourless mica grain is enclosed by olivine. In sample #463706-3 similar 128 colourless mica is found interstitially to medium grained olivine crystals.

Several xenoliths show evidence of fracturing, and the presence of carbonate-magnetite intergrowths in such fractures suggests that the xenoliths became disaggregated within the lamprophyre dyke during crustal deformation. This can be appreciated in Fig. 2a, showing secondary carbonate mineralization along extensive fracturing of olivine in xenolith #1 in sample #463715 connected to similar carbonate-Fe-oxide intergrowth in the matrix. Another example of this is presented in Fig. 2b (sample #463728), where carbonate-Fe-oxide intergrowth forms 'horns' at the edges of xenoliths #1 and #2 - probably representing growth in pressure shadows.

Tremolite and talc is coexisting with olivine in some of the altered portions of the xenoliths and provides evidence for premetamorphic alteration of at least parts of the olivine grains. A collection of micro- and macrodiamonds have been recovered from several bulk samples of the Qeqertaa dyke (Marmo et al., 2012) during exploration activities from 2007-2012.

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### 141 **3.** Analytical technique

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143 Minerals grains were analysed on standard 40 µm polished thin sections, using the JEOL 144 electron microprobe at the Institute of Geology and Geography, University of Copenhagen. All 145 elements in silicates were measured by WDS, with 20 s peak count time for Na, Mg, Fe, Si, and Ti, 146 while Cr. Ni, Ca and Al were measured with 40 s peak count time. Natural and synthetic standards 147 were measured at the beginning and at the end of each session. For traverses in spinel, an analytical 148 routine optimized for oxides was utilized and the elements analysed were Mg, Fe, Si, Ca, Ti, Cr, 149 Mn, Fe, Ni and Zn. Peak count time for Zn was 40 s and 10 s for remaining elements. Background 150 count time on either side of the peak was half that of peak count time for both silicates and spinels. 151 Table 1 in the online supplementary material lists a series of representative mineral data. The mineral data presented there represents the core compositions, typically 2-3 analyses, and for 152 153 orthopyroxene and garnet, an average of 4-6 analyses.

- 155 **4. Results**
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- 157 *4.1. Olivine chemistry*
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159 There is a large compositional variation in olivine. The overall range in Mg#  $(100 \text{xMg}/(\text{Mg}+\text{Fe}^{2+}))$  out of almost 600 analyses is from 80.3 to 94.6 as shown in the insert in Fig. 160 161 4. Ni varies from 1328 ppm to 4008 ppm (median value of 2727 ppm) and does not correlate with 162 Mg#. Because olivine composition cannot be related to the textural state of olivine, i.e. xenocrystic 163 or xenolithic (not shown), all olivine in the following is referred to as xenoliths. Fig. 4 also shows 164 the distribution of Mg# in olivine in 119 individual xenoliths, as presented in Table 1 (see online 165 supplementary material). While this data set represents core compositions, the range in Mg# is 166 similarly large, spanning Mg# 80-94. Neither of the data sets (all olivine analyses and xenolith 167 cores only) show a good correlation of Ni versus Mg# (see Fig. 4, insert). Several olivine grains 168 have been analysed along traverses from crystal rim to core. The data are presented in Fig. 5 in 169 terms of the variations in Mg# and Ni contents. Fig. 5a shows a traverse over about 0.3 mm in the 170 core of a large olivine crystal. The variation in Mg# is moderate in the range 93.4-94.1, while Ni is 171 in the range 2295-2955 ppm. These ranges are only slightly larger than what is known from olivine 172 in fresh, unaltered mantle xenoliths from Tertiary volcanics and dykes elsewhere in Greenland 173 (Bernstein et al., 1998, 2006).

Some Qeqertaa xenoliths have olivine crystals, such as samples #qq1 and #qq4 (Fig. 5b and 5c), that show similarly consistent Mg# and Ni concentrations over more than one millimetre traverse and with only a modest zoning with small decreases in Mg# over the outer 0.1 mm of the crystal. These crystals have only weakly altered olivine rims (#qq1, Fig. 5b) or no detectable alteration (#qq4-olivine2, Fig. 5c). Other samples contain olivine grains, which show more pronounced zoning, such as #qq2a-olivine1 and #qq3-olivine1 (Fig. 5d and 5e), with core compositions of 93.4 and 92.0, respectively, and rim compositions of 90.3 and 87.7. Ni varies from an average value of 181 about 2500 ppm in the high Mg# region, decreasing to 2000 and then to 1600 ppm at the grain 182 edges. These two olivine crystals are also typical of the more altered versions of olivine, with thick 183 0.2-0.3 mm alteration rims marked by brown coloration (Fig. 3a). The colour seems to stem from 184 minute oxide inclusions, typically less than 1 µm, in the olivine, mainly Fe-oxide, as judged from 185 microprobe data.

One olivine crystal was analysed with a traverse (Fig. 5f) that runs from crystal core to the edge against a spinel grain (Fig. 7a). The olivine crystal is homogeneous apart from one fracture, which coincides with a small excursion from a steady level at around Mg# 92.9 to 92.2, accompanied by a small decrease in Ni. The olivine grain terminates at a thin veneer (20  $\mu$ m wide) of mica that surrounds the spinel grain (Fig. 7a), and the olivine attains its high Mg# and Ni content approaching this contact (Fig. 5f).

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# 193 4.2. Spinel chemistry

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As discussed above, irregular spinel grains or aggregates of magnetite and chromian magnetite are found along cracks and veins in the olivine xenoliths. Spinel textures and occurrence suggests that these irregular grains and aggregates are of secondary origin. Spinel grains with similar texture and composition are also ubiquitous in the matrix and will not be discussed further.

Spinel of likely primary origin is found in portions of the xenoliths, where alteration has been less intense. Some spinel grains interpreted as relic primary spinel are present in the centre of irregular masses or aggregates of iron oxide grains. On the basis of microscopy and back-scatter electronic images, it is apparent that two basic types of relic, primary spinel grains occur: 1) some (rare) with recognizable primary grains boundaries, only narrow alteration rims and a less modified core, and 2) more intensely altered grains, with obscured primary grain boundaries, often with overgrowths of chromian magnetite.

206 The best preserved spinel grains are found as two small (0.1-0.3 mm) slightly translucent grains 207 completely enclosed in a large (12 mm) olivine grain (Fig. 6a). The compositional variation of the 208 core of this olivine grain is presented in Fig. 5a. The two spinel grains are compositionally similar 209 with Cr#, calculated as Cr# = (100xCr/(Cr+Al)), in the spinel cores of 60.0 ±0.5, increasing to a 210 maximum of about 62 at grain edges (Fig. 6b). Mg# and Al#, calculated as Al# = (100xAl/(Fe<sup>3+</sup>+Al+Cr)), also show restricted ranges at around 56 and 39, respectively, decreasing 211 slightly at grain edges. Fe<sup>3+</sup># is very low, mostly between 1 and 2, and increasing slightly to 3-4 at 212 213 grain edges. ZnO shows slight variation around 0.5 wt.%, while both NiO and TiO<sub>2</sub> is at or below 214 detection limit (Fig. 6d). As examples of the relatively well-preserved spinels of type 1), but with 215 pronounced alteration, Figs. 7a and 8a show two spinel grains in the 100 µm size range. Texturally 216 the two grains are similar, with a translucent core, and a pitted and opaque rim. Spinel grain #qq4bsp1 (Fig. 7a) is rounded and anhedral, typical for spinel grains in xenoliths of cratonic mantle 217 218 peridotite, while grain #qq3-sp1 (Fig. 8a) is subhedral. Fine-grained mica aggregates separate the 219 spinel from hosting olivine grains. Chemically, the two spinel grains share some characteristics with relatively constant levels of Cr#, Mg#, Fe<sup>3+</sup>#, and Al# in the core, that change markedly at the grain 220 edges towards elevated Cr# and Fe<sup>3+</sup># and lower Mg# and Al#. This zoning is also pronounced for 221 222 ZnO, which varies from about 1 wt.% in the centre of the spinel grains to 3 wt.% towards the rim 223 for #qq4-sp1 (Fig. 7d). For spinel #qq3-sp1, the variation and absolute concentrations in ZnO is less 224 extreme with about 0.4-0.7 wt.% (Fig. 8d). For titanium and nickel, core concentrations are  $\sim 0.1$ 225 wt.% increasing to 0.5 wt.% (TiO<sub>2</sub>) and ~ 0.3 wt.% (NiO) at the crystal rim (Fig. 7d). Spinel #qq3-226 sp1 again shows less variation, with 0.2-0.3 wt.% TiO<sub>2</sub> and  $\leq$  0.1 wt.% NiO (Fig. 8d). MnO follows 227 the pattern of ZnO at similar concentration levels (not shown) for all analysed spinel grains.

As an example of spinels of type 2), which are more altered and anhedral, Fig. 9 illustrates one grain from sample #qq4, with a short analytical traverse from grain boundary to some way into the core. As for the type 1 spinels in Figs. 7 and 8, a mosaic of mica crystals completely surrounds this spinel, separating it from the host olivine. In this case the mica zone is 50-100 µm wide. The spinel

is opaque and the backscatter electron image (Fig. 9a) does not reveal significant zoning, although the rounded shape of the primary spinel can be detected inside the ragged rim. In contrast to the type 1 spinel grains, type 2 shows little variation from core to rim, and instead has extreme Cr#, approaching 100. Mg# is low (<20) and Fe<sup>3+</sup># high (>50). Concentrations of minor elements ZnO and TiO<sub>2</sub> are considerably less variable than for type 1 spinel, and typically with values at 0.7-1.0 wt.%, while NiO is low between 0.1 and 0.2 wt.% (Fig. 9d).

238 From the data presented above it is clear that all spinel grains have undergone variable degrees 239 of chemical modification since the lamprophyre hosting the xenoliths was emplaced. Only a few 240 spinel grains have been analysed with electron microprobe traverses, so it is important to use a 241 chemical parameter that can distinguish between highly altered spinel cores and the less altered cores that potentially retain their primary Cr#. One such parameter is  $Fe^{3+}$ #, which varies from 1.3 242 243 to 98.0 in Oegertaa samples. This is in marked contrast to unaltered and unzoned spinel in mantle xenoliths in Tertiary lavas and dykes in West and East Greenland, which all have  $Fe^{3+}$ # <10 in 244 245 spinels that span a Cr# range of 25-95 (Fig. 10). By contrast, Table 1 in the online supplementary material lists all spinel data from Qeqertaa that have  $Fe^{3+}$ # <10; only 20 samples have such low 246 247 values.

Fig. 11 illustrates the compositions of Qeqertaa spinel with Fe<sup>3+</sup># <10. The markedly lower Mg# at a given Cr#, compared to the xenolith suites of Ubekendt Ejland and Wiedemann Fjord, is an indication of lower temperature Fe-Mg exchange with olivine and other silicates in the Qeqertaa spinels. The Qeqertaa samples yield olivine-spinel Fe-Mg exchange temperatures of 400-600°C (Ballhaus et al., 1991; Sack and Ghiorso, 1991), which is substantially lower than Ubekendt Ejland (833-960°C; Bernstein et al., 2006) and Wiedemann Fjord (650-995°C; Bernstein et al., 1998).

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255 *4.3. Orthopyroxene chemistry* 

257 The three orthopyroxene grains from three individual xenoliths show a restricted variation, with 258 Mg# spanning 92.7-93.7, and with  $Cr_2O_3$  and  $Al_2O_3$  levels at 0.41-0.52 wt.% and 0.79-0.85 wt.%, 259 respectively (Table 1, online supplementary material). CaO is ca. 1.1 wt.% for two samples, while 260 the remaining sample has only 0.3 wt.% CaO. The three dunite xenoliths that contain orthopyroxene 261 have no garnet, but the high Cr# (26-30) of all three orthopyroxene grains suggests that they have 262 equilibrated with garnet, as orthopyroxene from garnet-free peridotite xenoliths have significantly 263 lower Cr#, mostly less than 20 (Fig. 12). An important note here is that the distinction between 264 orthopyroxene from garnet-bearing and garnet-free peridotite disappears for orthopyroxene with 265 extremely low contents of Al<sub>2</sub>O<sub>3</sub> (<0.2 wt.%), that have variable Cr#, from 4-96 (Fig. 12). This is 266 possibly an artefact of poor analytical accuracy or extreme Al depletion during mantle melting and 267 melt extraction in spinel stability field (Bernstein et al., 2007; Stachel et al., 1998). However, the 268 distinction appears robust for orthopyroxene with Al<sub>2</sub>O<sub>3</sub> exceeding 0.2 wt.%.

Because of the lack of coexisting phases, such as garnet or clinopyroxene, it is not possible to calculate equilibrium temperatures for the garnet-bearing assemblages, and it is indeed questionable if such calculations would be meaningful, given that the xenoliths were subjected to amphibolite facies metamorphism after emplacement of the Qeqertaa dyke.

- 273
- 274 5. Discussion
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# 276 5.1. Metamorphic overprinting

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The strongly zoned nature of olivine and chrome spinel from the xenoliths of Qeqertaa is a typical aspect of prograde metamorphism of altered peridotite (e.g. Evans and Frost, 1975; Nozaka, 2003; Trommsdorff et al., 1998; Vance and Dungan, 1977). The Qeqertaa olivines with brown, inclusion-rich grain margins show textural similarity to hydrothermally altered olivine xenocrysts and xenoliths from Venetia kimberlites, South Africa (Stripp et al., 2006), where thin talc rims form 283 on serpentinised olivine grains. In a study of olivine compositional variation in Chugoku peridotite 284 (Japan), which has been subjected to steep local metamorphic gradients, Nozaka (2003) 285 demonstrates how primary olivine with Mg# around 91 can attain both higher (to 97.6) and lower 286 (to 86) Mg# during prograde reactions. The assemblage at Qeqertaa of coexisting olivine, tremolite 287 and talc is analogous to metamorphic zone 3 of Nozaka, (2003, and references therein), where 288 essentially all olivine is metamorphic. The metamorphic olivine in Chugoku peridotites forms overgrowths, along distinct grain boundaries and 'healed' cracks or veins, where olivine replaces 289 290 serpentine. Magnetite-free serpentine is thought to be the precursor of high-Mg# olivine, while low-291 Mg# olivine is thought to crystallize from magnetite-bearing serpentine. The olivine in Qegertaa 292 xenoliths always shows normal zoning with low-Mg# zones crowded with minute Fe-oxide 293 inclusions. These low-Mg# rims are thus likely to represent recrystallized, partly serpentinised 294 olivine with Fe-oxide grains remaining from the hydrothermally reacted olivine.

295 In Qegertaa xenoliths, all olivine grains show some reaction along grain boundaries, evident 296 from the presence of either hydrous phases, such as talc, or fine-grained Fe-oxide inclusions. 297 However, many olivine grain centres are colourless, transparent and inclusion-free down to the 298 resolution of the electron microprobe. These olivine cores coincide with maximum Mg# in the 299 individual olivine and suggest that the cores represent primary olivine that escaped extensive 300 serpentinisation. Likewise, the typical coarse protogranular texture (Fig. 3) suggests that the 301 Qegertaa xenoliths are not entirely recrystallized from serpentine or talc during prograde 302 metamorphism, as such recrystallization commonly forms equigranular olivine aggregates or highly 303 elongate olivine resembling spinifex texture (e.g. Trommsdorff et al., 1998). Another piece of 304 evidence for the colourless olivine to have escaped the initial serpentinization is the presence of 305 inclusions of pale, inclusion-free phlogopite crystals that are in strong contrast to the dark-brown, 306 inclusion-rich mica phenocrysts or xenocrysts in the groundmass.

The relatively robust nature of chromite makes these a potential powerful recorder of alteration
processes (e.g. Barnes, 2000; Evans and Frost, 1975; Kimball, 1990). The types of chemical zoning

309 depicted in Figs. 6-9 can be explained in terms of hydrothermal alteration followed by prograde 310 metamorphism from primary chromite with slightly altered crystal rims to magnetite rimmed spinel 311 grains with equilibrated cores. The high ZnO (mostly at 0.4-3.0 wt.%) present in all spinel grains 312 with electron probe traverses, show that even spinel cores have been modified by metamorphic 313 reactions, because primary spinels have ZnO at the 0.1 wt.% level, at least in komatiite flows 314 (Barnes, 2000). The exception is the spinel portrayed in Fig. 6a, which perhaps escaped strong 315 modification. Certainly, some spinel has been altered to magnetite, which is found in cracks and 316 veins, as well as along olivine grain boundaries (Fig. 3). This suggests at least some degree of early 317 partial serpentinisation and later recrystallization of olivine, which would then leave magnetite 318 interstitially between olivine crystals as seen in Fig. 3.

319 The spinel grains in 463722 and #qq-4b (Figs. 6 and 7) are morphologically the least altered 320 spinel grains of those analysed. The lack of a thick, euhedral Fe-spinel jacket suggests that these 321 grains have remained relatively undisturbed during metamorphism. While the zoning in the two 322 spinel grains in 463722 is very modest, #qq-4b shows a more pronounced decrease of magnesium 323 and aluminium towards the rim and around the transecting crack, which is typical for chromite 324 equilibrating with olivine, talc, or ferroan magnesite (for Mg) and chlorite (for Al) (Barnes, 2000). 325 In the case of the Qegertaa xenoliths, the samples lack chlorite. However, Cr-Al exchange between 326 spinel and mica, as in the following simplified reaction, would decrease the Al content of spinel:

327

328 
$$MgAl_2O_4 + 2KMg_3CrSi_3O_{10}(OH)_2 = 3MgCr_2O_4 + 2KMg_3AlSi_3O_{10}(OH)_2$$

329

Instead or in addition, metamorphic reactions forming mica from talc + olivine + aluminous
spinel + fluid, as in the following simplified example, could also explain the high Cr# in remaining
Qeqertaa spinels:

334  $7Mg_3Si_4O_{10}(OH)_2 + 2Mg_2SiO_4 + 10MgAlCrO_4 + 5K_2O_{(aq)} + 3H_2O = 10KMg_3AlSi_3O_{10}(OH)_2 + 3H_2O = 10KMg_3O_{10}(OH)_2 + 3H_2O = 10KMg_3O_{10}(OH)_2 + 3H_2O = 10KMg_3O_{10}(OH)_2 + 3H_2O = 10KM$ 

335

$$5 Mg Cr_2 O_4$$

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The occurrence of one or both of these reactions is consistent with the phlogopite-rich composition of the mica that coats the spinel in for example Fig. 7a) at the end of line-1 (see supplementary data Table 1).

Following Barnes' (2000) study, serpentinisation of dunite xenoliths and olivine in the lamprophyre matrix results in decomposition of olivine and release of Zn. Chromite absorbs Zn, resulting in a steep concentration profile from high ZnO at altered chromite rims to very low concentration (<0.1 wt.%) at unaltered chromite cores. Prograde metamorphism to amphibolite facies subsequently redistributes Zn in the chromite grains and tends to homogenize concentration differences, which in turn also results in elevated Zn in grains that have retained their primary Cr# (Barnes, 2000).

348 In a more extreme case, such as in Fig. 9 (#qq4, line4) aluminium is completely lost, along with 349 most of the magnesium. The overgrowth of Fe-rich spinel exhibits crystal faces, but still contains 350 appreciable amounts of Cr. In fact, only a few of the analysed chrome spinel grains have pure 351 magnetite rims. In a plot of all spinel analyses in terms of their trivalent cations (Fig. 13) these highly altered grains (as in Fig. 9), and altered spinel rims (Figs. 7-8) plot along the Cr-Fe<sup>3+</sup> join, 352 clustering at  $Cr_{30}Fe^{3+}_{70}$ - $Cr_{50}Fe^{3+}_{50}$  and connecting to the main body of spinel data along the Al-Cr 353 join at low (generally <10%) Fe<sup>3+</sup>. These intermediate spinel compositions suggest extensive solid 354 solution between the spinel end-member components (Fe,Mg)Cr<sub>2</sub>O<sub>4</sub>, (Fe,Mg)Al<sub>2</sub>O<sub>4</sub> and 355 356 (Fe,Mg)Fe<sub>2</sub>O<sub>4</sub> and thus equilibration temperatures above 600°C according to Sack and Ghiorso 357 (1991). At temperatures at or below 550°C the solid solution stability field is significantly reduced 358 by miscibility gaps, which expand with decreasing temperature, resulting in formation of coexisting

359 chromite and Cr-poor magnetite (see also Barnes, 2000). The presence of intermediate360 compositions in the Qeqertaa xenoliths suggests crystallization above the solvus

Fig. 10 shows that most spinel analyses have high  $Fe^{3+}$ # (>10) reflecting the effects of hydrothermal alteration and/or amphibolite facies metamorphism. However, even spinel with  $Fe^{3+}$ # (>10 have lost their primary Mg# as seen in Fig. 11. The least altered Qeqertaa xenoliths plot along the metamorphic trend identified by Frost and Evans (1975). As in most alpine peridotite massifs, Fe-Mg exchange between spinel and olivine has reduced spinel Mg#.

Primary spinel Cr# can in some cases be preserved in metamorphosed peridotites. The range of Cr# in Qeqertaa spinels overlaps with that of Ubekendt Ejland and Wiedemann Fjord xenolith suites, raising the possibility that some crystals retain primary Cr#'s. However, Qeqertaa xenolith spinels plot along the metamorphic Cr# versus Mg# trend of Evans and Frost (1975) for spinels in chlorite-bearing metaperidotites. Very high Cr# and low Mg# in metamorphic spinels were also observed by Barnes and Roeder (2001), further suggesting that Qeqertaa spinel Cr#'s may have been modified by metamorphic reactions, perhaps to some degree even for spinels with low Fe<sup>3+</sup>#.

In summary, the combined evidence from olivine and spinel points to a history of partial replacement of olivine by serpentine during hydrothermal alteration, followed by prograde metamorphism to amphibolite facies, as suggested by the presence of recrystallized olivine rims, the character of zoned chrome spinel, and olivine-spinel Fe-Mg thermometry.

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- 378

#### 379 *5.2. Primary olivine compositions*

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Considering olivine cores only, the Qeqertaa xenoliths have an average Mg# of 92.6 with a median Mg# of 92.8. Given the considerable zoning, these values are probably minimum estimates of the average and median, values of primary Mg#, because (a) some apparent olivine cores may be from olivine in which the plane of the thin section is parallel to and close to one edge of the crystal, and therefore have broad areas of low-Mg#, and (b) even some of the larger, clear grains may be
neoblasts, crystallized from completely serpentinised primary olivine. In any case, olivines from
Qeqertaa xenoliths have highly refractory compositions that are typical for dunite and harzburgite
xenolith suites from the lithospheric mantle beneath Archaean cratons (e.g. Bernstein et al., 1998,
2006, 2007; Boyd, 1989; Boyd et al., 1997; Canil, 2004; Lee and Rudnick, 1999; Menzies, 1990;
Pearson et al. 2003; Wittig, 2008).

391 The large range in olivine Ni concentrations (1328 ppm to 4008 ppm) portrayed in Fig. 4 and in 392 detail for a subset of individual olivine crystals in Fig. 5, is not easily explained. Some of the range 393 may reflect the redistribution of Ni during partial serpentinization and subsequent prograde 394 metamorphism as discussed above. One likely example is shown in Fig. 5d, in which the 395 recrystallized olivine rim shows substantially lower Mg# and variable but overall decreasing Ni 396 content compared to olivine core. However, even for colourless, inclusion-free olivine grains or 397 olivine cores, there appears to be considerable variation in Ni content. Our microprobe traverses of 398 seemingly unaltered olivine cores with near-constant Mg# reveal Ni variation spanning 2000-3000 399 ppm over few hundred microns (Fig. 5b, c and f), although one grain (Fig. 5a) shows a much tighter 400 variation in Ni with values between 2400 and 2900 ppm. One potential explanation for such 401 variation could be that all olivine is of metamorphic origin, which in turn implies that the low-402 temperature hydrothermal alteration altered the entire peridotite mineral assemblage prior to the 403 prograde metamorphism. We find this to be implausible not only on textural grounds as described 404 in section 5.1 but also because rare, large, pale mica crystals in the dunite xenoliths are free of the 405 magnetite inclusions that dominate the altered mica crystals in the groundmass. We find it unlikely 406 that a phlogopite crystal would maintain its textural integrity if it were engulfed in completely 407 serpentinized dunite.

During our microprobe work on the olivine, we have not detected any inhomogeneity by backscatter imagery and the origin of the Ni variation is therefore uncertain. While it could stem from minute sulphide inclusions, we also note that the majority of the analytical values are within the 411 normal range for olivine from olivine-rich, residual mantle peridotites (2000-3500 ppm; e.g., 412 Bodinier and Godard, 2003). We note that the range in Ni for the Qegertaa xenolithic olivine is 413 similar to that observed for other xenolith suites in the North Atlantic craton which may suggest 414 that this is a common feature (e.g. Bernstein et al. 1998, 2006; Wittig et al., 2008). One possibility 415 is that early (prior to peridotite entrainment in lamprophyre) melt-rock reaction could be responsible 416 for some of the decrease in Ni content of olivine, such as is observed in dunite replacing harzburgite 417 in the Bay of Island ophiolite (Suhr et al. 2003). However, we do not currently have trace element 418 data to test if melt-rock reactions were significant in this case. Variable Ni concentrations, with very 419 low values in some parts of olivine crystals, could also be due to the presence of sulfides during 420 peridotite recrystallization in the mantle. This is observed in sulfide-rich dunites from Oman 421 (Negishi et al. 2012). However, no sulphides have been observed in any of the Qegertaa xenoliths. 422 Another potential process that might account for the large variability of Ni in olivine is nickel 423 redistribution during early pervasive serpentinisation, followed by later prograde recrystallisation. 424 We reiterate that the large Ni variation in olivine appears to be a common feature in Greenlandic 425 xenolith suites, regardless of their emplacement age or post-emplacement thermal history. A 426 systematic study of nickel content in olivine for all Greenlandic xenolith suites could address this 427 question.

428 With respect to the nearly monomineralic composition of the Oegertaa xenoliths, they are similar 429 to the shallow, garnet-free, spinel dunites from Ubekendt Ejland, and the olivine-rich, 430 orthopyroxene-poor spinel harzburgites from Wiedemann Fjord (average ca. 12 wt.% 431 orthopyroxene). All three suites have similar average olivine compositions of Mg# 92.6-92.8 432 (Bernstein et al., 1998, 2006, 2007). The growing body of data on cratonic mantle xenoliths from 433 Greenland suggests that such olivine-rich mantle may be more common here than in other cratons, 434 and perhaps is the most abundant lithology in the shallow, cratonic mantle beneath some parts of 435 Greenland. Sample collections from Southwest Greenland (some 300-800 km south of Disko Bay) 436 have peridotite xenolith suites typically ranging from 75-100% modal olivine, with compositions

averaging Mg# 92.5-92.8 (Bizzarro and Stevenson, 2003; Garrit, 2000; Wittig et al., 2008). In other
cratons, such as Kaapvaal, Tanzania, Siberia, and Slave, mantle xenolith suites typically have lower
modal olivine and higher orthopyroxene, with ranges of 40-80% olivine and 20-60%
orthopyroxene, plus additional spinel, clinopyroxene and garnet (see compilations of e.g. Griffin et
al., 2003; Herzberg, 1993; Lee, 2006; Pearson et al., 2003).

442 It has long been clear that the high Mg# of olivine in cratonic mantle peridotite exceeds that of 443 olivine from Phanerozoic abyssal peridotite, most orogenic peridotite massifs and most peridotite 444 from arcs (Bonatti and Michael, 1989; Boyd, 1989; Boyd and Mertzman, 1987; Menzies 1990; 445 Nixon and Boyd, 1973) and that this elevated Mg# in olivine and bulk rock compositions likely 446 stems from higher extents of partial melting in the Archaean (Boyd, 1989; Herzberg, 2010; Jordan, 447 1975; O'Hara et al., 1975). The nature of the melting processes has on the other hand been subject 448 to much debate over the last couple of decades, mainly because the orthopyroxene-rich mantle 449 peridotites beneath Kaapvaal and some other cratons, such as Yakutia in Siberia, for many years 450 were considered representative of cratonic mantle. The high proportion of orthopyroxene (often >40 451 wt.%) in these peridotite xenoliths is considered inconsistent with an origin as residues of melt 452 extraction from primitive upper mantle compositions (e.g. Herzberg, 1993; Kelemen et al., 1998; 453 Kesson and Ringwood, 1989; Walter, 1998).

454 Following the discovery of depleted orthopyroxene-poor xenoliths from Greenland and some 455 other cratons (Bernstein et al., 1998, 2007; Boyd and Canil, 1997; Larsen, 1982) it has become 456 widely accepted that such high-Mg#, orthopyroxene poor harzburgites and dunites, and olivine + 457 spinel inclusions in diamonds, can be viewed as archetypical cratonic mantle peridotite (e.g. 458 Bernstein et al., 2007; Pearson and Wittig, 2008) formed by melt extraction of 37-45% (e.g. 459 Herzberg, 2004). The modal composition of orthopyroxene-poor harzburgite and dunite cratonic 460 xenoliths and their high Mg# suggest that they are residues of polybaric decompression melting 461 starting at 4 to 6 GPa and extending to less than 3 GPa (Bernstein et al., 1998, 2006; Herzberg, 462 2004; Kelemen et al., 1998; Walter, 2003). Depending on the nature of melting and melt extraction

463 ("equilibrium porous flow" versus "fractional melting"), this may be consistent with the observation 464 that the trace element composition of SCLM xenoliths from several cratons suggests melting at a shallow depth (< 3GPa; e.g. Canil, 2004; Wittig et al., 2008). Alternatively, high Mg# and other 465 466 indications of extreme melt depletion could be the cumulative result of multiple stages, each with a 467 moderate degree of melt extraction. The uniform olivine Mg# of 92.6-92.8 of the cratonic high Mg# dunite may have been controlled by the exhaustion of orthopyroxene during melt extraction, 468 469 limiting the maximum extent of melt depletion to about 40% in most cases, regardless of the tectonic environment (Bernstein et al., 2007). 470

471 Likewise, there is a growing consensus that the orthopyroxene-rich nature of mantle peridotite 472 beneath e.g. Kaapvaal, is a result of silica addition through melt-rock reaction, in which silica-rich 473 melts react with a high-Mg# dunite protolith, perhaps in the hanging wall of a subduction zone 474 (Gibson et al., 2008; Griffin et al., 2009; Kelemen et al., 1998; Kesson and Ringwood, 1989; Lee, 475 2006; Pearson and Wittig, 2008; Rudnick et al., 1994; Lee et al., 2011). Indeed, the data and 476 interpretations of Hanghøj et al. (2001) and Bernstein et al. (2007) suggest that Al as well as Si has 477 been added to dunite protoliths in most cratonic harzburgites, and that some cratonic lherzolites are 478 also refertilised dunites, modified by addition of Ca, Fe, Al, Si, and probably many other elements.

479 Pressure and temperature at the time of xenolith entrainment can be calculated for many garnet-480 bearing peridotite xenoliths. Pressures indicate depths of equilibration in the order of 2.5-7 GPa or 481 about 75-220 km depth (e.g. Lee, 2006). Disregarding xenoliths with clear signs of metasomatic 482 overprinting by a basaltic/basanitic or carbonatitic melt (i.e. presence of abundant diopside, 483 amphibole, mica, carbonate, rutile etc.), there is a surprisingly constant and high Mg# of olivine in 484 cratonic mantle, from 91.5-94.0 for most cratons, with averages spanning 92.0 to 93.0 (e.g. Gaul et al., 2000; Griffin et al., 2003; Pearson and Wittig, 2008), which do not correlate with depth of 485 486 equilibration. These values are similar to depleted, garnet-free spinel peridotite xenoliths from the 487 cratons, which also have average olivine Mg# of 92.5-92.8 (Bernstein et al., 2007).

488 As noted above, the bulk composition of most garnet-bearing cratonic mantle xenoliths reflects 489 low pressure melting in the absence of garnet (e.g. Canil and Wei, 1992; Kelemen et al., 1998; 490 Stachel et al., 1998) despite their deep residence at the time of entrainment. The trend of bulk 491 compositions, with correlated Ca and heavy rare earth element concentrations, demonstrate that few 492 if any cratonic peridotites contain residual garnet. Instead, most garnets in the cratonic upper mantle 493 must be metamorphic in origin (Kelemen et al., 1998). This interpretation requires that low-pressure 494 peridotite residues of decompression melting have been transported to depth at some later stage, 495 possibly during collision of tectonic plates leading to stacking of the depleted and hence buoyant 496 dunitic restite (e.g. Helmstaedt and Schulze, 1989; Gray and Pysklywec, 2010) or via ascent and 497 accumulation of buoyant, Fe-poor peridotite diapirs (e.g., Oxburgh and Parmentier, 1977, 1978).

498 In this light, the presence of garnet-bearing dunite with average olivine Mg# of 92.6 in the 499 Qegertaa suite, considered together with the garnet-free Ubekendt and Weidemann xenolith suites, 500 shows that by Palaeoproterozoic time, the mantle beneath this part of the North Atlantic craton 501 included regionally extensive high Mg# dunite extending from depths within the spinel peridotite 502 stability field (Bernstein et al., 2006), deep into the garnet peridotite stability field, and indeed into 503 the diamond stability field as documented by the presence of diamonds in the Qeqertaa dyke 504 (Marmo et al., 2012). Along typical cratonic conductive geotherms (surface heat flow of 40-50  $mW/m^2$ ), this results in a vertical distribution of high-Mg# dunite over 150 km of the lithospheric 505 506 mantle.

507

### 508 6. Conclusions

509

510 We have shown that yet another SCLM xenolith suite from Greenland records consistently high 511 Mg# in olivine. The Qeqertaa xenoliths have average olivine Mg# of 92.6 and a median value of 512 92.8, which appears to be the dominating composition for SCLM in the North Atlantic craton.

The presence of garnet in five xenoliths, suggests an equilibration pressure greater than 2.5 GPa (>75 km depth). The presence of diamonds in the Qeqertaa dyke demonstrates that the SCLM in this region must have been more than 150 km thick prior to the Palaeoproterozoic transport of the xenoliths into the crust.

The after emplacement in the crust, Qeqertaa xenoliths likely equilibrated at temperatures slightly above 600°C, as reflected in their spinel compositions, during amphibolite facies metamorphism in the crust. The Cr# versus Mg# trend of spinel from Qeqertaa is different than for xenoliths from Ubekendt Ejland and Wiedemann Fjord (Bernstein et al., 1998, 2006), although they probably shared a similar origin in highly depleted, residual dunites.

522 Unlike spinel Mg#'s, which are typically modified during metamorphism, spinel Cr#'s can in some cases preserve primary, residual compositions. Values of  $Fe^{3+}\# < 10$  in some Qegertaa 523 524 spinels suggest that primary Cr# may have been preserved in a few cases. However, the Qegertaa 525 xenolith spinels plot along the metamorphic Cr# versus Mg# trend for chlorite-bearing peridotites 526 identified by Evans and Frost (1975). Our samples do not contain chlorite, but they do contain 527 metamorphic mica separating spinels from host olivine crystals. This suggests that even spinel Cr# 528 can be modified by open behaviour during amphibolite facies metamorphism. Thus, care must be 529 taken when interpreting the geological formation environment of metamorphic mantle rocks, in 530 terms of their spinel composition.

The surprisingly monotonous lithology in the 100% dunite Qeqertaa xenolith suite further supports the hypothesis that much of the cratonic mantle is composed of low pressure residues of high degrees of decompression melting, limited by the exhaustion of orthopyroxene (Bernstein et al., 2007). The Qeqertaa data are similar to xenolith data from other areas of the North Atlantic craton, as well as some other cratons as seen in Fig. 14, which supports the hypothesis that olivinerich dunites and harzburgites with Mg# around 92.8 represent the pristine composition of SCLM, prior to refertilization via melt-rock reaction.

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772	Online supplementary material
773	
774	Table 1. Electron microprobe data for the Qeqertaa xenolith suite.
775	
776	Figure captions:
777	
778	Fig. 1. Simplified geological map over the north-eastern Disko Bay region, showing the location of
779	the island Qeqertaa in the northern Rodebay domain. Qeqertaa is situated a few kilometres south of
780	the border of the Atâ tonalite. After Garde and Steenfelt (1999).
781	
782	Fig. 2. Examples of xenoliths and olivine megacrysts in the Qeqertaa xenolith suite. a) Sample
783	#463715 xenoliths #1 and #2. Note lobate olivine xenolith (#1) with small (1 mm) rounded
784	orthopyroxene inclusion and right hand side of xenolith fractured by carbonate-Fe-oxide veins. b)
785	Sample #463728 showing spherical dunite xenoliths with small (<1 mm) orthopyroxene inclusion
786	in xenolith #2. Note the carbonate (colourless mineral) filled pressure shadows between the two
787	xenoliths. c) Sample #463711 with rounded garnet inclusion in dunite. Olivine grain is >20 mm.

Garnet partly replaced by kelyphite. d) Sample #463713, showing typical dense clustering of small
xenoliths. Xenolith #3 contains small spinel grains (0.1 mm), while the xenoliths #1, #2, and #4 are
monomineralic dunite, apart from alteration minerals. Note darker (brown) olivine margins in
xenolith #1.

Fig. 3. Xenolith qq-2 with typical coarse, protogranular texture demonstrating the lack of foliation
or preferred orientation of the olivine grains (a) plane-polarized light; b) crossed-polarized light).
The grain size range for olivine is large, from 2 mm to more than 15 mm. The sample also
illustrates the nearly monomineralic nature of the xenolith suite from Qeqertaa.

797

Fig. 4. Range in olivine compositions as reflected by Mg#  $(100 \times Mg/(Mg+Fe^{2+}))$  and Ni content in ppm. Histogram shows data for 119 individual olivine xenoliths, while insert shows all olivine analyses.

801

Fig. 5. Representative examples of microprobe traverses across six olivine grains, showing thevariation in Mg# and Ni content.

804

Fig. 6. a) Backscatter electron image of two spinel grains enclosed in a fractured olivine grain from sample #463722. The lines refer to microprobe analyses as presented merged in panels below. b) Cr# = (100xCr/(Cr+Al) and Mg# =  $(100xMg/Mg+Fe^{2+})$ ; d) Fe<sup>3+</sup># =  $(100xFe^{3+}/(Fe^{3+}+Al+Cr))$  and Al# =  $(100xAl/(Fe^{3+}+Al+Cr))$ . Note the weak zoning only in the outer few tens of micrometres and TiO<sub>2</sub> and NiO around detection limit.

810

Fig. 7. a) Backscatter electron image of zoned spinel from sample #qq-4b, with lines referring to microprobe analyses as presented in panels below (line-1 is a traverse in olivine and presented in Fig. 5f). b)-d) show chemical variation along the analytical traverse b-c. Note the strong zoning from a relatively homogeneous core to a narrow rim with changes in all depicted chemical parameters. Also note the chemical modification along the crack in the spinel grains, perpendicular to the analytical traverse.

Fig. 8. a) Backscatter electron image of zoned spinel from sample qq-3, with line a-b referring to microprobe analyses as presented in panels below. b)-d) show chemical variation along the analytical traverse b-c (see caption to Fig. 6 for chemical parameters). The data reveals strong zoning from a relatively homogeneous core to a narrow rim with changes in all major element parameters. For the minor elements, Zn, Ni and Ti, there is little variation from core to rim (d).

823

Fig. 9. a) Backscatter electron image of zoned spinel from sample qq-4b, with line a-b referring to microprobe analyses as presented in panels below. b)-d) show chemical variation along analytical traverse a-b (see caption to Fig. 6 for chemical parameters). There is relatively little variation along the traverse, compared to the less altered spinel grains in Figs. 6-8. Note that Cr# is at 100 in b) and Al# is at 0 in c).

829

Fig. 10. Chemical variation in terms of Cr# and Fe<sup>3+</sup># comparing all spinel analyses from Qeqertaa xenolith suite with compositions of spinel in mantle xenoliths from Ubekendt Ejland (UE - dark grey field), West Greenland and Wiedemann Fjord (W – light coloured field), East Greenland (data from Bernstein et al., 1998, 2006 and unpublished data). Qeqertaa spinel data lying in one of the fields with Fe<sup>3+</sup># less than 10 may have retained their primary Cr#, while those lying outside have been substantially modified during metamorphism.

836

Fig. 11. Spinel from Qeqertaa xenoliths, with the most altered compositions removed (see text and Fig. 10) in terms of Cr# versus Mg#, compared to spinel from Ubekendt Ejland (UE) and Wiedemann Fjord (W) suites. Qeqertaa xenoliths almost span the entire range in Cr#, but have substantially lower Mg#, which is a reflection of lower equilibration temperatures compared to the Ubekendt and Weidemann suites.

843 Fig. 12. Composition of orthopyroxene (in the only three samples found to contain orthopyroxene), 844 in terms of Cr# and Mg#. Also shown are compositional field for orthopyroxene from Greenlandic garnet-bearing xenoliths (Sarfartoq-Maniitsoq region; Garrit, 2000) and from garnet-free, spinel-845 846 bearing xenoliths from Ubekendt Eiland, Wiedemann Fjord and Sarfartoq-Maniitsoq (Bernstein et 847 al., 1998, 2006; Garrit, 2000, respectively). Only orthopyroxene with Al<sub>2</sub>O<sub>3</sub>>0.2 wt.% is included in 848 the bodies of data for garnet-free xenoliths. Some orthopyroxene with Al<sub>2</sub>O<sub>3</sub><0.2 wt.% show a much greater variation in Cr# (stippled field), which is possibly an artefact of poor analytical 849 850 accuracy close to the detection limit.

851

Fig. 13. Spinel compositions from analytical traverses by electron microprobe in five spinel grains
from the Qeqertaa xenolith suite, compared with unaltered spinel in mantle xenoliths from
Ubekendt Ejland, West Greenland (Bernstein et al., 2006). The three components represent atomic
proportions referring to the spinel formula, with Fe<sup>3+</sup> calculated assuming stochiometry.

856

Fig. 14. Cr# in spinel versus Mg# in olivine from different cratonic xenolith suites. Qeqertaa
xenoliths plot on top of this array and their Cr# covers the entire range. Diamond inclusions on the
other hand are restricted to Cr# around 90. The background data are from the literature as follows:
Ubekendt (Bernstein et al., 2006), diamond inclusions (Stachel et al., 1998), Tanzania (Rudnick et
al., 1994), Kaapvaal (Herzberg, 2004), Sarfartoq (Bizzarro and Stevenson, 2003; Garrit, 2000),
Wiedemann (Bernstein et al., 1998) and OSMA (Arai, 1994).

Figure 1 Click here to download high resolution image











#### Figure 6 Click here to download high resolution image



# Figure 7 Click here to download high resolution image



# Figure 8 Click here to download high resolution image





Figure 10 Click here to download high resolution image









## Figure 14 Click here to download high resolution image



Background dataset for online publication only Click here to download Background dataset for online publication only: Table 1 Microprobe data.xlsx