# Paradoxical co-existing base metal sulphides in the mantle: the multi-event record preserved in Loch Roag peridotite xenoliths, North Atlantic Craton

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[1] **Abbreviations**: North Atlantic Craton (NAC), Great Glen Fault (GGF), North Atlantic Igneous Province (NAIP), British Palaeogene Igneous Province (BPIP), subcontinental lithospheric mantle (SCLM), platinum-group elements (PGE), highly siderophile elements (HSE), base metal sulphide (BMS)

1    **Abstract**

2    The role of the subcontinental lithospheric mantle as a source of precious metals for mafic magmas

3    is contentious, and given the chalcophile nature of metals such as the platinum-group elements

4    (PGE), Se, Te, Re, Cu and Au, the mobility of these metals is intimately linked with that of sulphur.

5    Hence the age, stability and host phases of chalcophile metals in the subcontinental lithospheric

6    mantle may be of critical importance. We investigate the sulphide mineralogy and sulphide *in situ*

7    trace element compositions in base metal sulphides (BMS) in a suite of spinel lherzolite mantle

8    xenoliths from northwest Scotland (Loch Roag, Isle of Lewis). This area straddles the margin of the

9    North Atlantic Craton which has been overprinted by a Palaeoproterozoic orogenic belt, and occurs

10   in a region which has undergone a series of magmatic events as recent as the Eocene.

11   We identify two populations of co-existing BMS within a single spinel lherzolite xenolith (LR80) and

12   which may also be recognised in the peridotite xenolith suite as a whole. Both populations consist of

13   a mixture of Fe-Ni-Cu sulphide minerals, and we distinguished between these according to BMS

14   texture, petrographic setting (i.e., location within the xenolith in terms of 'interstitial' or within

15   feldspar-spinel symplectites, as demonstrated by X-ray Computed Microtomography) and *in situ*

16   trace element composition. Group A BMS are coarse, metasomatic, have low concentrations of total

17   PGE (< 40 ppm) and high $(Re/Os)_N$ (ranging 1 to 400). Group B BMS strictly occur within symplectites

18   of spinel and feldspar, are finer and rounded droplets, with micron-scale PtS (cooperite), high overall

19   total PGE concentrations (15-800 ppm) and low $(Re/Os)_N$ ranging 0.04 to 2. Group B BMS are

20   sometimes observed to coexist with apatite, and both the Group B BMS and apatite can preserve

21   rounded micron-scale Ca-carbonate inclusions indicative of sulphide-carbonate-phosphate

22   immiscibility. This carbonate-phosphate metasomatic association appears to be important in

23   forming PGE-rich sulphide liquids although the precise mechanism for this remains obscure. As a

24   consequence of their position within the symplectites, Group B BMS are particularly vulnerable to

25   being incorporated in ascending silicate magmas (either by melting or physical entrainment) during

26      mantle-derived magmatism. Based on the cross-cutting relationships of the symplectites through the

27      Loch Roag spinel lherzolite xenoliths, it is possible to infer the relative ages of each metasomatic

28      BMS population and an attempt is made to tally these with major tectono-magmatic events for the

29      region. Thus it may ultimately allow for the temporal and spatial mapping of the chalcophile

30      metallogenic budget of the lithospheric mantle.

## 1. Introduction

Mantle xenoliths provide a direct but incomplete view into the lithospheric mantle and the composite and complex magmatic and/or metasomatic events that it has experienced over time (e.g. Pearson *et al.,* 2003). Interest in the subcontinental lithospheric mantle (SCLM) and its role in hosting metals such as Cu, Mo, Se, Te, the platinum-group elements (PGE) and Au, has been discussed in the literature for over 30 years (cf. Mitchell and Keays 1981; Groves *et al.,* 1987; Groves & Bierlein, 2007; Arndt, 2013, and references therein). Many of these metals are strongly chalcophile and the ability of the shallow mantle to store or release them is thought to be largely dependent upon the nature and behaviour of their main hosts, Fe-Ni-Cu sulphides and platinum-group minerals (PGM) (e.g., Lorand *et al.,* 2008; 2013; Lorand & Luguet, 2016; Luguet & Reisberg; 2016).

The composition of the lithospheric mantle in terms of PGE and other chalcophile metals has been widely documented over the course of several decades, and studied in the context of lithospheric age, tectonic/geodynamic setting and the presence and composition of the late veneer event (e.g., Jagoutz *et al.*, 1979; Morgan 1986; Pattou *et al.,* 1996; Alard *et al.,* 2000; Holzheid *et al.,* 2000). Many studies centred on bulk rock geochemistry (e.g., Maier *et al.,* 2012) may be prone to significant nugget effects due to the heterogeneous distribution of PGE-bearing microphases (Lorand *et al.,* 2013), and thus detailed investigations that combine base metal sulphide petrography and mineral compositions (e.g., for Re, PGE, Se, Te and semi-metals) and isotopic systematics (particularly for the Re-Os system) are vital in order to assess the true complexity of the upper mantle sulphur and chalcophile element reservoir (e.g., Alard *et al.,* 2000, 2005; Aulbach *et al.,* 2009; González-Jiménez *et al.,* 2014; Griffin *et al.,* 2002, 2004; Harvey *et al.,* 2010; Lorand *et al.,* 1990, 2003, 2008, 2010; Luguet *et al.,* 2003, 2004; Marchesi *et al.,* 2013; Szabo *et al.,* 1995; Wainwright *et al.*, 2015).

Advances of *in situ* analytical techniques have led to a deeper understanding of how accessory particles that comprise aggregates of Fe-Ni-Cu sulphide minerals (hereafter termed "base metal

56  sulphides" (BMS)) and platinum-group minerals (PGM) control the chalcophile element

57  geochemistry of the upper mantle (Lorand *et al.*, 2013; Lorand & Luguet, 2016 and references

58  therein). This has led to the acceptance that several populations of BMS may be present in upper

59  mantle samples. Most commonly, this is manifest as: (i) rounded BMS with compositions similar to

60  monosulphide solid solution (Mss) that can occur in intergranular positions or as inclusions in olivine

61  and/orthopyroxene; and (ii) Cu-rich BMS that are restricted to intergranular sites. These two major

62  populations generally have distinct PGE systematics – Mss-type BMS are Os-, Ir-, Ru- and Rh-

63  enriched with unradiogenic Os-isotopic compositions, while Cu-Ni-rich BMS are typically Pd (and

64  sometimes Au) enriched with comparably radiogenic Os-isotopic compositions (Burton *et al.*, 1999;

65  Alard *et al.*, 2002, 2011; Lorand *et al.*, 2013 and references therein). Mss-type sulphides are most

66  commonly interpreted as residual sulphide remaining after partial melting while the Cu-rich BMS

67  formed as a result of melt infiltration or metasomatism (e.g. Guo *et al.*, 1999; Alard *et al.*, 2000;

68  Lorand & Alard, 2001; Aulbach *et al.*, 2004; Lorand & Grégoire, 2006; Powell & O'Reilly, 2007; Zheng

69  *et al.*, 2007; Alard *et al.*, 2011; Saunders *et al.*, 2015; Luguet and Reisberg; 2016).

70  A study by Delpech *et al.* (2012) on Kerguelen mantle xenoliths found that interstitial BMS may be

71  produced by melt-rock reactions during the percolation of volatile-enriched alkaline-silicate small-

72  melt fractions (i.e., metasomatism) and/or by sulphidization reactions of supercritical (S- or $CO_2$-rich)

73  fluids with mantle silicates (olivine). Delpech *et al.* (2012) argued that these BMS formed during

74  refertilisation of harzburgitic mantle by large volumes of alkaline-silicate melts then subsequently by

75  small-volume volatile-rich silicate melts, and finally by small volumes of carbonate-rich fluids. The

76  latter events were associated with a distinct generation of metasomatic BMS, and reveal complex

77  carbonate-sulphide associations in the mantle lithosphere (Menzies & Dupuy, 1991; Grégoire *et al.*,

78  2000; Lorand *et al.*, 2004; Moine *et al.*, 2004). Specifically, the population of BMS formed by

79  sulphidization reactions was selectively enriched in S, Cu, Pd, Pt and Os, and this evidence has since

80  been used to infer the geochemical fingerprints of sulphide crystallisation from carbonate- or $CO_2$-

81    rich fluids during mantle metasomatism in an off-craton environment (Delpech *et al.*, 2012; Lorand

82    *et al.*, 2013; Lorand & Luguet, 2016).

83    The complexity of the upper mantle sulphur budget reflected by multiple BMS populations is widely

84    recognised within the mantle xenolith research community. However, the implications of this for the

85    supply of chalcophile elements to magmas that are either sourced from, or that transit, the SCLM,

86    and hence the regional implications for orthomagmatic sulphide-hosted Ni-Cu-PGE mineral deposits,

87    are not so widely established. Generalised assumptions about the nature of mantle sources for

88    chalcophile elements may be inadvertently oversimplified if reference to observed mantle lithologies

89    and sulphide mineralogy is overlooked for a particular geographical region. When assessing the

90    metallogenic signature of a region, and its potential to produce and host magmatic sulphide

91    mineralisation, a coherent and holistic understanding of the nature and setting of refractory or

92    fusible BMS populations in the lithospheric mantle (as recorded by mantle xenoliths) must be

93    considered. In particular, this must take into account the vulnerability of BMS (as per population and

94    textural setting) to melting and remobilisation/redistribution into/by ascending asthenosphere-

95    derived magmas, (e.g., Bedini *et al.*, 1997; Pearson *et al.*, 2003; Lorand *et al.*, 2004; Lorand & Luguet,

96    2016; Luguet & Reisberg, 2016; Hughes *et al.,* 2015a). This is pertinent in the prediction of the

97    precious or critical metal characteristics of sulphide mineralisation – for example, (Pt/Pd) ratios and

98    Co abundances (Hughes *et al.,* 2015a, 2016).

99    In this study, we present *in-situ* analyses for PGE, Au, Re and semi-metals (As, Sb, Se, Te and Bi)for

100   two distinct populations of intergranular BMS within a single spinel lherzolite mantle xenolith

101   entrained within the Eocene-aged Loch Roag monchiquite dyke in NW Scotland. We compare the *in-

102   situ* BMS-hosted element data with bulk rock major and trace lithophile element and chalcophile

103   element data geochemistry for this, and other spinel lherzolite xenoliths from the same Loch Roag

104   suite (previously published in Hughes *et al.,* 2014, 2016). The Loch Roag dyke entrains xenoliths from

105   a fragment of the North Atlantic Craton (locally known as the Lewisian Gneiss Complex) and

106    probably represents Archaean SCLM underlying the long-lived marginal region at the craton edge

107    that was significantly re-worked in the Palaeoproterozoic.

108    *1.1 Geological setting*

109    Documented mantle xenolith localities in Scotland span five tectonic terranes (see Upton *et al.,* 2011

110    and references therein) with each terrane delineated by a major lithospheric lineament, such as the

111    Great Glen Fault (Fig. 1a). In the far NW of Scotland, the Archaean – Palaeoproterozoic Lewisian

112    Gneiss Complex makes up the British portion of the North Atlantic Craton (NAC), and is primarily

113    characterised by the exposed basement of the Caledonian foreland bounded to the east by the

114    Moine Thrust Zone (MTZ). The Lewisian Gneiss Complex comprises mid-late Archaean tonalite-

115    trondhjemite-granodiorite (TTG) gneisses, with minor mafic-ultramafic and metasedimentary

116    components, that have been reworked by several Late Archaean and Palaeoproterozoic tectonic

117    events – i.e., Late Palaeoproterozoic orogenesis correlated with both the Nagssugtoqidian and

118    Ketilidian-Makkovikian mobile belts in Greenland (e.g., Bridgwater *et al.,* 1973; Park & Tarny, 1987;

119    Park, 1994; Park, 1995; Baba, 2002; Kinny *et al.,* 2005a; Park, 2005; Goodenough *et al.,* 2013).

120    Early Palaeoproterozoic extension (c. 2.4 Ga) led to the formation of a large igneous province (LIP),

121    now represented by the Scourie Dyke Swarm (e.g., Davies & Heaman, 2014). These mafic-ultramafic

122    dykes represent the roots of this LIP, which presumably fed shallow intrusions and flood basalts at

123    the palaeo-surface. The combination of negative Nb-Ta-Ti anomalies, enriched Th and light rare

124    earth elements (REE) and negative $\gamma$Os found in the Scourie Dykes indicate a significant magmatic

125    component derived from partial melting of the SCLM (Hughes *et al.,* 2014). The c. 2.4 Ga Scourie

126    Dyke tectono-magmatic event coincides with a carbonatitic metasomatic event previously

127    recognised in the Loch Roag xenocryst assemblage by model Nd-isotopic ages (c. 2.3-2.5 Ga; Long *et*

128    *al.,* 1991) that may also be related to the carbonatitic intrusions in western Greenlandic NAC c. 2.6

129    Ga; Larsen & Rex, 1992 and references therein).

130    Elsewhere on the marginal cratonic portion of the Scottish lithosphere (i.e., north of the Great Glen

131    Fault, Fig. 1a) Neoproterozoic (c. 550 Ma) carbonatitic events have been identified based on

132    clinopyroxene Sr-Nd isotopic compositions of Streap Comlaidh and Rinibar mantle spinel lherzolite

133    xenoliths (e.g., Bonadiman *et al.,* 2008). Metasomatic clinopyroxenes can also be identified, using *in-*

134    *situ* trace element geochemistry, in the Loch Roag spinel lherzolites (Hughes *et al.,* 2015b),

135    corroborating the inferred carbonatite-related metasomatism by Long *et al.,* 1991, albeit in the Early

136    Palaeoproterozoic. Hence it is suggested that multiple carbonatitic metasomatic events, ranging in

137    age from the early Proterozoic to the late Neoproterozoic, are recorded by the Scottish marginal

138    cratonic SCLM and the timing of these events are broadly correlated with carbonatite and kimberlite

139    intrusions in the Greenlandic NAC (Larsen & Rex, 1992).

140    In the Palaeogene, the North Atlantic Igneous Province (NAIP) formed by the impingement of the

141    proto-Icelandic mantle plume beneath cratonic lithosphere. This rifted the NAC such that the British

142    portion of the NAC (Lewisian Gneiss Complex) became separated from the Greenlandic portion

143    during the opening of the North Atlantic and the onset of active continental rifting c. 62 Ma

144    (Saunders *et al.*, 1997). The British Palaeogene Igneous Province is the earliest magmatic expression

145    of the NAIP (in addition to that recorded in western Greenland and Baffin Island) and is developed

146    throughout the Hebrides on the west coast of Scotland, and in Northern Ireland (Saunders *et al.,*

147    1997).

148    *1.2 Loch Roag monchiquite dyke – host to the xenolith suite*

149    The 70cm wide Loch Roag monquichite dyke (a mafic lamprophyre with brown amphibole, Ti-augite,

150    olivine and biotite; see Gillespie and Styles, 1999) is host to the mantle xenoliths dealt with in this

151    study and sits on the leading edge of the rifted NAC (Fig. 1b). The dyke itself is mid-Eocene in age

152    ($^{40}Ar$-$^{39}Ar$ mica age, 45.2 ± 0.2 Ma; Faithfull *et al.*, 2012) and the youngest known magmatic event in

153    the UK, and is therefore entirely distinct from the c. 2.4 Ga Scourie Dyke Swarm. Whilst most mantle

154    xenolith-bearing dykes in western Europe south of Scandinavia pass through lithosphere that has

155 experienced Phanerozoic (Caledonian/Hercynian/Alpine) orogenesis, the lithosphere traversed by

156 the Loch Roag dyke has remained undeformed since the Mesoproterozoic (c.f., 1.6 Ga Laxfordian

157 event) as it sits outside of the Caledonian orogenic front. Hence this dyke contains a suite of upper

158 mantle and crustal xenoliths and xenocrysts, unusual in comparison to elsewhere in the wider UK

159 and Europe (Upton *et al.*, 1983). Namely, it comprises a diverse range of lithologies and megacrysts;

160 including spinel lherzolites, glimmerites, anorthosites/anorthoclasites, gabbros and syenite

161 xenoliths, phlogopite 'books', apatite and corundum xenocrysts (Upton *et al.*, 1983; Hunter & Upton,

162 1987; Menzies *et al.*, 1987; Menzies & Halliday, 1988; Long *et al.*, 1991; Upton *et al.*, 1999 and Upton

163 *et al.*, 2011).

### 1.3 Petrography and bulk geochemistry of the Loch Roag spinel lherzolite xenoliths

165 Detailed studies of the non-sulphide mineralogy, mineral chemistry, and bulk rock geochemistry and

166 isotopic compositions of the Loch Roag spinel lherzolite xenoliths have previously been documented

167 by Hunter & Upton (1987), Menzies *et al.* (1986) and Upton *et al.*, (2011 and references therein), and

168 recently revisited by Hughes *et al.* (2015b, 2016). In this contribution we summarise these studies to

169 provide substantive information important to the characterisation of the sulphide mineralogy and

170 chemistry and to the identification of different BMS populations.

171 The spinel lherzolite xenoliths are typically up to 4cm in diameter, slightly rounded in overall shape

172 and have an oxidised green-orange-brown 'rim' (normally up to 1 cm thick) at the contact with the

173 host dyke (Fig. 2a). Haematite and sulphate minerals (such as barite) are common in these halos and

174 are ascribed to reaction with of the peridotite during entrainment in the host dyke (e.g., Fig. 2a,

175 LR80 (1) thin section image). However, the central portions of the xenoliths comprise grey-coloured

176 peridotite unaffected by reaction with the host dyke. These 'unaltered' peridotite cores have sub-

177 equigranular, granoblastic and porphyroblastic textures with crystal sizes typically ranging 1 to 2 mm

178 although orthopyroxene porphyroblasts up to 10 mm in length are also observed. Due to their small

179 size, very few of the xenoliths have unaltered peridotite interiors sufficiently large enough for

180    effective sampling – thus two xenoliths 'LR80' and 'LR81' abound in the literature as these offer the

181    best opportunity for extensive and repeated sampling and analysis (both for bulk rock and *in situ*

182    techniques). These xenoliths were sliced into a series of 5-10 mm wide sections and this curated

183    material summarised in Upton *et al.* (2011) has been the focus of several studies since the 1980's

184    and this current work.

185    Olivine compositions in spinel lherzolite xenoliths LR80 and LR81 range $Fo_{89.8-88.7}$, with 0.3-0.4 ppm Ni

186    (Hunter and Upton, 1987). Clinopyroxenes are systematically $SiO_2$-richer but $Al_2O_3$-poorer when

187    compared to other Scottish lherzolite xenoliths (i.e., 54 wt.% vs. 51-52 wt.% $SiO_2$ and 4.2-4.7 wt.% vs.

188    5-8 wt.% $Al_2O_3$ respectively; Upton *et al.*, 2011). Mean orthopyroxene compositions are

189    approximately $En_{89}Fs_{10}Wo_1$ and these are relatively Al-poor in comparison to other Scottish

190    lherzolites (2.2-2.6 wt.% vs. 2.0-5.3 wt.% respectively $Al_2O_3$; Upton *et al.*, 2011).

191    Spinel grains appear 'corroded' and are surrounded by, and intergrown with, sodic-feldspars forming

192    a set of symplectite-like pockets (Fig. 2b-c) along spinel-clinopyroxene, clinopyroxene-olivine, and

193    olivine-olivine grain boundaries (Hunter & Upton, 1987; Upton *et al.*, 2011). Feldspars are

194    anorthoclase-oligoclase with a mean composition of $Or_{7.6}Ab_{80.8}An_{11.6}$ (Hunter & Upton, 1987; Upton

195    *et al.*, 2011). Spinel has 35-49 wt.% $Cr_2O_3$ (notably higher than other Scottish xenoliths which

196    typically have < 20 wt.%; Upton *et al.,* 2011) and in rare cases, very fine granular high-Cr spinel

197    (lacking Mg and Al) can be found as atoll-like features in the symplectites and nucleating on the edge

198    of the larger corroded Al- and Mg-bearing (hercynitic) spinel (Fig. 2c). All spinel and feldspar occur

199    within these 'symplectites'. In some cases, micrometric intergrowths of sodic-feldspar with Na-rich

200    clinopyroxene and olivine form a zone up to 250 µm wide surrounding the spinel-feldspar

201    symplectites, and in rare cases (typically areas on the outer margins of the xenoliths) melt

202    percolation recorded as finely crystalline ilmenite-chromite-plagioclase-biotite patches, may also be

203    observed following the path of the symplectites.

204    Bulk geochemistry of the Loch Roag lherzolites was first published in Menzies *et al.* (1986), but the

205    xenoliths have subsequently been resampled and reanalysed by Hughes *et al.* (2014, 2015b, 2016).

206    Due to the limited material available to work with, most powdered xenolith samples included some

207    proportion of the outer reaction rim described above, however in the case of sample LR80 (labelled

208    on Fig. 3), the xenolith was large enough that this reaction rim could be entirely removed prior to

209    powdering and a duplicate slice of unaltered LR80 material kept for *in situ* mineral analysis for the

210    purposes of this study.

211    Anhydrous bulk rock Cr/Al, Al/Si and Ca/Si ratios for Loch Roag lherzolites (Hughes *et al.*, 2015b) are

212    compared with harzburgites, lherzolites and wherlites from the North Atlantic Craton (NAC) keel in

213    west Greenland in Figures 3a and 3b. The latter have low Al/Si and Ca/Si and extremely variable

214    Cr/Al (Wittig *et al.,* 2010) relative to 'Primitive Upper Mantle' (PUM; McDonough & Sun, 1995). The

215    Loch Roag lherzolites form an intermediate group between Greenlandic and PUM compositions and

216    the elevated Ca/Si and Al/Si of Loch Roag suggests significant refertilisation. Comparing anhydrous

217    Cu vs. Cr/Al highlights a significant enrichment in Cu for all Loch Roag lherzolites (particularly LR80

218    which sampled only the unaltered interior of the xenolith) in comparison to both Greenlandic NAC

219    xenoliths and PUM.

220    Upton *et al.* (2011) used a simple melting model for Al and Mg in ortho- and clinopyroxene to

221    demonstrate that the majority of Scottish spinel lherzolite xenoliths (including Loch Roag) have

222    orthopyroxene compositions consistent with their being residual after melt extraction. In contrast,

223    the melting curve calculated for clinopyroxene does not fit the compositions observed in Loch Roag

224    xenoliths (and most other Scottish xenolith suites) and therefore the clinopyroxenes cannot be

225    described as residual. In addition, following studies into the relative abundances of Zr-Hf in

226    pyroxenes as an indicator of cryptic metasomatism (Downes *et al.,* 2015) the high Zr/Hf ratios of the

227    Loch Roag clinopyroxenes have been interpreted to indicate cryptic metasomatism of the spinel

228    lherzolites (Hughes *et al.,* 2015b).

229

## 2. Analytical techniques and methodology

### *2.1 Petrography and mineral chemistry analysis*

Petrographic studies on polished thin sections and polished blocks were employed to identify xenolith textures. Further examination, mapping and quantitative microanalysis was carried out on a Cambridge Instruments S360 scanning election microscope (SEM) at Cardiff University. Quantitative microanalyses were obtained using an Oxford Instruments INCA Energy EDS analyser attached to the SEM, with operating conditions set at 20kV and specimen calibration current of ~2 nA at a fixed working distance of 25mm. Analytical drift checks were carried out every 2 hours using the Co reference standard and a comprehensive suite of standards from MicroAnalysis Consultants Ltd were used to calibrate the EDS analyser. All Loch Roag SEM quantitative major element data (Fe, Ni, Cu, S) for individual sulphide minerals are in Supplementary Table A and a representative selection of these data are presented in Table 2.

Polished blocks were selected for laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) for sulphide trace element analysis. Time resolved analysis (TRA) by LA-ICP-MS was performed on BMS aggregates containing multiple sulphide minerals at Cardiff University on a New Wave Research UP213 UV laser system attached to a Thermo X Series 2 ICP-MS. Both line and spot analysis were used and independently calibrated, depending on the size of the BMS. For lines, a minimum length of ~80µm and a beam diameter of 15µm was used, with laser operating conditions of 10Hz frequency, 0.063 mJ at 4.98 Jcm$^{-2}$ and sample translation at 6µm sec$^{-1}$. For spot analysis, beam size was 40µm and the same laser operating conditions as for the line analyses were employed. BMS < 80µm diameter were only analysed by spot analysis. Acquisition times ranged 40 to 180s with a gas blank measured for 30s prior to laser ablation. Major element abundances (Fe, Ni, Cu, S) of the sulphide were measured by SEM prior to LA-ICP-MS, and $^{33}$S was used as an internal

253    standard for trace element calibration. Gas blank subtraction and internal standard corrections were

254    carried out on Thermo Plasmalab software.

255    Synthetic Ni-Fe-S quenched sulphide standards were used for LA-ICP-MS calibration, including S, Ni,

256    Fe and Cu as major elements, and Co, Zn, As, Se, Ru, Rh, Pd, Ag, Cd, Sb, Te, Re, Os, Ir, Pt, Au and Bi as

257    trace elements. The compositions and details of analytical methods for these standards are

258    presented in Prichard *et al.* (2013) and further procedural details are available in Smith *et al.* (2014).

259    Standards 1, 2 and 3 were used for calibration of Fe, Ni, Cu, Co and Zn, as well as matrix-matched

260    corrections for argide species, which interfere with light PGE isotopes ($^{59}Co^{40}Ar$, $^{61}Ni^{40}Ar$, $^{63}Cu^{40}Ar$,

261    $^{65}Cu^{40}Ar$ and $^{66}Zn^{40}Ar$). Standard 1 was used in corrections for $^{106}Cd$ on $^{106}Pd$ and $^{108}Cd$ on $^{108}Pd$.

262    Argide and isobaric-corrected standard data are presented in Supplementary Table B, for Ru, Rh and

263    Pd. Independent corrections for isotopes of the same element (e.g., $^{66}Zn^{40}Ar$ and $^{106}Cd$ on $^{106}Pd$, and

264    $^{108}Cd$ on $^{108}Pd$) showed < 20% (commonly < 5%) variance, indicating that the correction criteria are

265    appropriate. The accuracy for PGE and Au was checked by analysis of the Laflamme-Po724 standard

266    as an unknown against the Cardiff quenched sulphide standards (results in Supplementary Material

267    Table B). The small size of many sulphides prevented repeat analyses and therefore 1σ precision

268    based on TRA counting statistics are typically 2-16% (concentrations 10-100 ppm), 10-27% (1-10

269    ppm) and 23-80% (<1 ppm). A representative selection of TRA for BMS analysed are presented in the

270    Supplementary Material and all Loch Roag LA-ICP-MS sulphide data are reported in Supplementary

271    Table C. A representative selection of these data are presented in Table 3.

272    ***2.2 Element maps – estimations of the modal abundance of sulphide***

273    Whole thin-section element maps of the samples were collected on a Zeiss Sigma HD analytical SEM

274    outfitted with dual 150mm² active area EDS detectors at Cardiff University. This used a 20μm step-

275    size (400 μm² per pixel) and a pixel dwell time of 15ms in order to create effective phase maps for

276    pyroxenes, olivine, spinel, feldspars, sulphides, carbonates and phosphates (see Supplementary

277   Material for all images and maps – PNG files named 'LR80-' accordingly). These maps have previously

278   been published in Hughes *et al.* (2016).

279   The modal abundance of BMS (counted as total sulphide without differentiating between Ni, Fe, or

280   Cu end-member compositions) per thin section of LR80 was estimated in each case using the built-in

281   PhaseMap tool in Oxford Instruments Aztec Energy software, which accounts for the shape of the

282   BMS within each thin section. The modal abundances of BMS, along with other accessory and

283   modally-major minerals for each scanned thin section are provided in a Table 4 (note that section

284   numbers correspond to those of the phase maps presented in the Supplementary Material).

285   ***2.3 X-ray Computed Microtomography (μCT)***

286   X-ray computed microtomography (μCT) provides a non-destructive technique by which to establish

287   and visualise the internal characteristics of mantle xenoliths. This is particularly effective for rare

288   samples whereby preservation of material may be paramount for curation. μCT scanning for

289   geoscience applications was developed by Carlson *et al.* (2000) and Ketcham & Carlson (2001). It has

290   been further advanced to visualise sulphide minerals (e.g., Kyle & Ketcham, 2003; Kyle *et al.*, 2004;

291   Godel *et al.*, 2006; Godel *et al.*, 2013), and has been applied to meteorites (e.g., Kondo *et al.*, 1997),

292   diamondiferous eclogitic xenoliths (e.g., Schulze *et al.*, 1996; Richardson *et al.*, 2014; Howarth *et al.*,

293   2015) and diamonds (Jacob *et al.*, 2011; Agrosi *et al.*, 2016). The details surrounding μCT scanning

294   are given in Denison *et al.* (1997), Ketcham & Carlson (2001) and Mees *et al.* (2003).

295   Tomographic data from a slice and a 5mm sub-core of LR80 were acquired using a μCT instrument

296   designed and built at the University of Edinburgh. The instrument comprised a 10-160kV Feinfocus

297   transmission x-ray source, a MICOS UPR-160-Air rotary table and a Perkin Elmer XRD0822 1

298   megapixel flat panel amorphous silicon detector with a Gd2O2S:Tb scintillator, operated by control

299   software developed in-house. In total 2000 projections, each the average of two exposures of two

300   seconds were collected through a 360° sample rotation, using radiation generated at a peak energy

301    of 80kV and 2.8W target power. Tomographic slices were reconstructed by filtered back projection

302    using Octopus 8.7 (Vlassenbroek *et al.*, 2010) and visualised in 2D and 3D using Fiji and Avizo 9

303    software.

304

305

306    **3. Results**

307    ***3.1 BMS petrography***

308    One sample (LR80) was large enough (approximately 6cm diameter of 'unaltered' core) to be cut

309    into slices, subsequently sampled by 8 thin sections and polished blocks, and petrographically

310    mapped (e.g., Fig. 2 and supplementary material whole section scans). Thus, LR80 provided a rare

311    opportunity to document the locations and petrography of BMS, including relationships between

312    different sulphide minerals, using SEM backscattered electron (BSE) imaging. One thin section from a

313    second xenolith, LR90, contained additional BMS within a symplectite pocket (see below) and these

314    were also studied. BMS were classified according to size, location, relationships with surrounding

315    non-sulphide minerals, BMS texture (relationship between constituent sulphide minerals making up

316    each BMS grain, with reference made to textural descriptions and classifications as first defined by

317    Lorand & Conquéré, 1983; Dromgoole & Pasteris, 1987; Szabo & Bodnar, 1995 and Guo *et al.*, 1999)

318    and compositions.

319    All BMS occur as intergranular components in the Loch Roag peridotites and no wholly enclosed

320    BMS inclusions were found. Using the classification criteria outlined above, two principal BMS

321    groups can be distinguished (see Table5). Group A BMS represent ~70% of the BMS grains observed

322    and/or analysed. They are coarse (generally 50-500 μm) and interstitial to olivine or pyroxene (Fig.

323    4a), often occurring at protogranular triple junctions (e.g., Fig. 4b), and without any systematic

324    association with a specific modally-major/minor mineral. EDS element mapping across three thin

325    sections of xenolith LR80 (see Supplementary Material) shows no enrichment in Ca, Na or P around

326    these BMS (c.f. the Group B BMS below). Detailed BSE SEM images of the Group A BMS reveal

327    internal textures (Fig. 5) with flame-like intergrowths of pyrrhotite and pentlandite (that resemble

328    those formed by high temperature sulphide exsolution of Mss; Lorand & Luguet, 2016), massive,

329    granular pentlandite and cross-hatched zones of chalcopyrite. The proportion of chalcopyrite within

330    a given BMS grain can be quite variable among the Group A BMS (cf. Fig. 5a-b, c) ranging from 0% to

331    14% (see Table 5).

332    By contrast, Group B BMS (~30% of the total number of BMS grains) are systematically associated

333    with the spinel-feldspar symplectites that occur throughout the LR80 xenolith (Fig. 4c) and in

334    symplectite pockets within the thin section from sample LR90 as well. Group B BMS typically appear

335    as droplet-like features, generally < 100 μm enclosed within the feldspar component of symplectites

336    (which surround the skeletal spinel component of symplectites; Fig. 6a-b, or rarely occur within

337    feldspar that feeds into micrometric intergrowths with Na-rich clinopyroxene and olivine form a

338    zone up to 250 μm wide surrounding the spinel-feldspar symplectites, Fig. 6d). Proportions of the

339    major sulphide minerals present in Group B BMS are summarised in Table 5. In some cases cooperite

340    (Pt-sulphide) has exsolved from BMS and formed a discrete platinum-group mineral (PGM) phase,

341    often associated with chalcopyrite (Fig. 6c-d). These PGM (up to 3μm long) are only observed in

342    group B BMS. Sometimes Group B BMS have a spongy appearance due to their incorporation of

343    multiple non-sulphide inclusions (serpentinite and $CaCO_3$ < 30μm; Fig. 6e-f). Serpentine-filled

344    inclusions are generally polygonal in shape, whilst $CaCO_3$ inclusions are rounded. These spongy BMS

345    are also < 100 μm in diameter and closely resemble the droplet-like appearance of their non-

346    inclusion bearing counterparts, although we note that the former tend to have a lower modal

347    abundance of chalcopyrite (2% for inclusion-bearing BMS vs. 8% for inclusion-absent Group B BMS).

348    Whether this is a real enrichment in Cu or a sampling bias induced by the small number of inclusion-

349    bearing BMS and the random nature of sectioning is unclear.

350     A discontinuous vein of apatite runs through the xenolith (LR80), and also contains BMS (Figure 7a).

351     Apatite crystals are 50-200 μm in size, irregularly shaped and typically associated with $CaCO_3$ and

352     feldspar of a composition identical to that of the symplectite pockets. Droplet-like BMS up to 150

353     μm diameter (occasionally with apatite inclusions < 10μm diameter) occur within this vein (Fig. 7b).

354     These BMS can have $CaCO_3$ inclusions (as well as apatite inclusions) and have similar sizes, shapes

355     and mineral textures to the other Group B BMS. Apatites display fine spongy texture with abundant

356     inclusions of $CaCO_3$ (where analysable, these are typically < 5μm, and can be < 1μm) and less

357     common sub-micron-scale Ni-Fe sulphide inclusions (Fig. 7c). This produces an unusual immiscibility

358     texture between phosphate, carbonate and sulphide. Very fine skeletal apatite crystals (up to 5 μm

359     long) also occur in the feldspar of the vein surrounding the spongy larger apatite crystals (Fig. 7c).

360     ***3.2 Xenolith three-dimensional textures and structures - μCT***

361     For the purposes of this study we aim to qualitatively establish the degree of interconnectivity of the

362     spinel-feldspar symplectites throughout the LR80 xenolith. This will help to establish the pathways

363     available to sulphide liquids in the sample, and the relationships between the two main populations

364     of BMS through the 3D visualisation of μCT results. Figure 8 shows an example of a 2D slice of the

365     μCT data (Fig. 8a) and 3D reconstruction μCT freeze-frames (Fig. 8b-e) generated from the same

366     polished blocks of sample LR80 used for petrographic studies (SEM and LA-ICP-MS) in this

367     investigation. In Figures 8b-c we have highlighted spinel (as a tracer for the symplectite portion)

368     within a polished block approximately 3cm diameter, by digitally removing the highest density phase

369     (BMS) and gradually stripping the lower density silicates (olivine, clinopyroxene, orthopyroxene and

370     feldspar) from the view. The accompanying supplementary material contains a video of this process.

371     The three dimensional distribution of spinel defines a distinct fabric within the xenolith (Fig. 8c) and

372     hence demonstrates that the xenolith is slightly sheared. This feature was not apparent before the

373     application of X-ray μCT scanning.

374    Following further processing of the µCT data, we have highlighted both the spinels and the lowest

375    density minerals in the xenolith – serpentinite (which our microscopic observations show to be of a

376    low modal abundance in the xenolith), and feldspar (within the symplectites). Figure 8d shows a sub-

377    region of a µCT scan with spinel highlighted in blue. At this smaller scale the lineation defined by

378    spinel is less apparent, however it does demonstrate internal networks of symplectites within the

379    xenolith. By displaying the low-density feldspars in this sub-region as a coloured semi-transparent

380    shell, we reveal the interconnectivity of the spinel-feldspar symplectites in LR80 (Fig. 8e). µCT

381    volumes were segmented using a global threshold to separate high density minerals (spinel and

382    BMS) from low density minerals (feldspar in the symplectites). Using this method, partial overlap

383    between spinel and BMS phases was unavoidable, but separation of symplectitic feldspar from these

384    phases was reliable. For visualisation, the separated binarised volumes of the spinel and BMS are

385    presented as volume renderings. The feldspars in the symplectites were further classified using the

386    "label" algorithm in Avizo to identify voxels in contact with each other (by either a face, edge or

387    vertex) so that they are labelled with a discrete colour to demonstrate connectivity through the

388    volume. The symplectites were then converted to a surface mesh and visualised as semi-transparent

389    structures to illustrate their relationship to spinel and BMS. For example, the grey-green shell shows

390    low-density voxels (i.e., feldspars) that are interconnected, and similarly the light red, purple, blue

391    and brown shells show more localised interconnectivity of the feldspars surrounding spinel in the

392    symplectites. This demonstrates that the spinel-feldspar symplectites form an open system through

393    the spinel lherzolite xenoliths of Loch Roag and hence preserve a fossil network of open pathways

394    for fluid/melt migration in the lithospheric mantle.

395    ***3.3 BMS geochemistry***

396    Quantitative SEM (with EDS measurements) are compiled in Table 2 and LA-ICP-MS data have been

397    compiled in Table 3 (the latter representing 75 *in situ* analyses of BMS grains in the Loch Roag spinel

398    lherzolite xenolith LR80 along with 8 analyses from a separate spinel lherzolite xenolith LR90, which

399    is texturally and mineralogically similar to LR80). The major sulphide mineral or mixture of sulphide

400    minerals ablated in each analysis are given in Table 3. Data are presented in Figures 9-11 and were

401    classified according to the BMS petrography (as outlined in Section 3.1) and their trace element

402    compositions determined by LA-ICP-MS. Hence Figures 9-11 refer to groups A and B BMS.

403    None of the laser data comprise 100% single sulphide minerals, but a small subset of the data

404    produce analyses with Fe, Ni and Cu concentrations within 96% of end member chalcopyrite and

405    within 95% of end member pyrrhotite (Ni-poor mss). One Group A analysis has 98% of the Ni

406    expected for end member pentlandite and two Group B analyses have Ni corresponding to 87-89%

407    of end member pentlandite (both termed hereafter pentlandite-88). The remainder are more

408    complex mixtures. Mixed laser analyses from both BMS groups overlap according to metal/S,

409    Fe/(Fe+Ni+Cu) and Ni/(Ni+Cu+Fe) ratios (Figure 9a-c). The larger grain size of Group A BMS allowed

410    specific analyses of coarse chalcopyrite and more chalcopyrite-rich mixtures, which leads to a wide

411    range of Cu/(Cu+Ni+Fe) ratios (0 to 0.52) compared to Group B (0 to 0.11), but this is a sampling bias

412    controlled by sulphide mineral size and there is substantial overlap in the Cu abundance of both

413    groups (Table 5) with no trend defined by the major element data (Table 2). However when Cu (from

414    the LA-ICP-MS dataset) is plotted against total PGE (Os+Ir+Ru+Rh+Pt+Pd) the two BMS groups are

415    clearly separated. Furthermore there is no correlation between Cu concentration vs PGE

416    concentration (Figure 9d) despite the overlap in Cu concentrations. 90% of the Group A BMS have

417    total PGE < 10ppm and 22% of Group A BMS have total PGE concentrations < 1ppm. Group B BMS

418    always have >15ppm total PGE and there is no systematic relationship between total PGE and Cu for

419    either BMS group.

420    Laser analyses with near end member compositions are plotted on chondrite normalised multi-

421    element diagrams in Figure 10a. Chalcopyrite is only available for Group A and is characterised by

422    very low concentrations of all PGE and Au. The normalised data reveal clear differences between the

423    PGE, Re and Au compositions of Ni-poor mss and pentlandite in Group A and Group B. In Group A,

424    Ni-poor mss and pentlandite both contain very low concentrations of Ir-group PGE (IPGE) and Rh

425    (Fig. 10a). The Group A pentlandite analysis shows enrichment in Pt and Pd compared to the Ni-poor

426    mss (($Pd/Ir$)$_N$ = 21.7 and 0.82 respectively). For Group B, PGE concentrations in both major sulphides

427    are higher than their equivalents in Group A. Analyses of Ni-poor mss and pentlandite-88 (both

428    Group B) produce flat normalised profiles (> 10 x chondrite) from Os to Rh. The Ni-poor mss displays

429    a strong depletion in Pt and Pd compared with the pentlandite-88 which is enriched in Pd, with a

430    variable negative Pt anomaly (Fig. 10a).

431    Collective spidergram plots for all Group A and all Group B BMS are shown in Figures 10b and 10c

432    respectively and from this figure it is clear that many of the features in the mixed patterns reflect

433    varying proportions of the individual and member component sulphide minerals. An exception to

434    this generalisation is that normalised patterns for Group B sulphides show both positive and

435    negative Pt anomalies (($Pt/Ir$)$_N$ 0.02-11.3 and ($Pt/Pd$)$_N$ 0.10-442). Negative anomalies are linked with

436    pentlandite (Fig. 10a) but strong positive anomalies are not observed in any of the sulphide end

437    members. Time resolved spectra (TRA) from LA-ICP-MS analyses with positive Pt anomalies (see

438    supplementary material for examples) show extreme spikes in Pt abundance along the laser line that

439    are integrated into the combined signal. These therefore corroborate instances where micro-

440    particles of cooperite (PtS) have been observed in the SEM images (e.g., Fig. 6c-d) and have

441    subsequently been sampled by the laser. Conversely, the absence of visual PGM, and the complete

442    lack of strong positive Pt anomalies in all Group A analyses by LA-ICP-MS suggests that cooperite or

443    any other PGM are entirely absent from this BMS population.

444    On a plot of ($Pd/Ir$)$_N$ vs. ($Os/Ir$)$_N$ (Fig. 11a) Group B BMS display almost three orders of magnitude

445    variation in ($Pd/Ir$)$_N$ (0.02-11.5) along a restricted range of ($Os/Ir$)$_N$ (0.84-1.54). Group A BMS extend

446    this vertical ($Pd/Ir$)$_N$ array upwards but also scatter either side of it (($Os/Ir$)$_N$ 0.18-8.7). Delpeche *et*

447    *al.*, (2012) observed a similar vertical array in Kerguelen peridotites but with consistent scatter only

448    to $(Os/Ir)_N$ greater than 1. The low $(Os/Ir)_N$ found in part of the Group A dataset was not found at

449    Kerguelen.

450    $(Re/Os)_N$ values are >1 in all the Group A end member sulphides and <1 in the Group B Ni-poor mss

451    and pentlandite-88 (Fig. 10a). This is reflected in the mixtures where 47 out of the 52 mixed Group A

452    analyses have $(Re/Os)_N$ values >1 (Group A range = 0.82-188) whereas 17 out of the 23 Group B

453    mixed analyses have $(Re/Os)_N$ <1 (Group B range = 0.01-1.37). $(Re/Os)_N$ is not affected by the Cu

454    content of the BMS with the groups clearly separated at equivalent Cu concentrations (Fig. 11b).

455    Group A and B BMS overlap in terms of S/Se ratios but the range for Group B (S/Se = 1950-3440)

456    clusters more tightly around the primitive mantle value of 3300 (Sun and McDonough 1995) whereas

457    Group A has a much wider range (S/Se = 1960-5680). When S/Se is plotted versus Te (Fig. 11c) it is

458    clear that Groups A and B follow different trends. Group A BMS may be both S-rich and Te-poor

459    compared with Group B. Tellurium concentrations for both groups are anti-correlated with Cu and

460    the trend of Te enrichment in very Cu-rich BMS observed by Delpeche *et al.*,(2012) is not found in

461    either BMS group at Loch Roag (Fig. 11d).

462

463

464    **4. Discussion**

465    The position of the Lewisian Gneiss Complex on the rifted edge of the North Atlantic Craton and the

466    multiple orogenic events recorded in this region led Hughes *et al.* (2015b) to suggest that the

467    Lewisian portion of the NAC has long been the margin of the craton itself. This means that it is

468    particularly vulnerable to metasomatism and refertilisation during orogenic events, unlike the

469    central keel portions of the craton which are characteristically depleted (e.g., Pearson *et al.* 2003;

470    Wittig *et al.*, 2010). This is illustrated in Figure 3 where the Loch Roag peridotites are enriched in Ca,

471    Al and notably Cu, compared to the West Greenland portion of the NAC.  Thus, Loch Roag xenoliths

472     cannot be regarded as truly 'cratonic', rather as 'marginal cratonic' at best. This provides an exciting

473     opportunity to assess the metallogenic metasomatic and refertilisation history of this portion of the

474     SCLM on the margin of the NAC as recorded by mantle BMS populations. As noted earlier, unlike

475     much of Europe south of the Caledonian front, this part of the SCLM has remained undeformed

476     since the mid Proterozoic.

477     ***4.1 Multiple populations of metasomatic BMS***

478     We have established, on the basis of petrographic setting (Table 5) and trace element geochemistry,

479     that two discrete populations of BMS are present in the Loch Roag peridotites, and specifically that

480     these co-exist within a single xenolith. Both groups of BMS show sulphide mineral textures similar to

481     those formed by high temperature exsolution of Mss and Iss through progressive cooling and

482     subsequent sub-solidus re-equilibration and very similar textures have been widely identified in

483     other mantle BMS (Alard *et al.*, 2000, 2011; Aulbach *et al.*, 2004; Lorand & Grégoire, 2006; Luguet

484     and Reisberg; 2016). The isolated nature and the absence of symplectite zones around Group A BMS

485     coupled with signficant overlap in the major element compositions of both groups (reflected by

486     Fe/(Fe+Ni+Cu) and Ni/(Fe+Ni+Cu) ratios; Fig. 9 and Table 2) precludes the possibility that one group

487     reflects the partial melting and mobilisation of the other. During incongruent partial melting of BMS,

488     the Cu-rich portion would be mobilised first as the lowest temperature sulphide, thus leaving a

489     Fe(Ni)-rich residue and forming a Cu-Ni-rich liquid (Holwell & McDonald, 2010; Lorand & Luguet,

490     2016 and references therein). If Group B BMS formed from partial melting of Group A, Group B BMS

491     ought to be systematically Cu-rich – and vice versa. This is not evident in our analyses.

492     As demonstrated in Figure 10, Group A and Group B end member minerals and mixed BMS analyses

493     have notably different PGE concentrations. Whilst subtleties in the PGE patterns per analysis may be

494     noted for Cu- or Ni-rich mixtures in each group, this fundamental PGE-rich vs PGE-poor

495     categorisation is robust irrespective of the proportions of individual sulphide minerals incorporated

496     into each BMS analysis. The trace element chemistries of Group A (e.g. $(Re/Os)_N$ >1, low IPGE,

497     $(Pt/Ir)_N$ >1, $(Pd/Ir)_N$ >1) and Group B (e.g. $(Re/Os)_N$ <1, high IPGE and variable $(Pt/Ir)_N$ and $(Pd/Ir)_N$)

498     have also been observed before and respectively conform to the Type 2 and Type 1 BMS of Alard *et*

499     *al.*, (2000). Presented on their own, the PGE signatures for Loch Roag Group A closely resemble Cu-

500     enriched BMS formed by melt infiltration or metasomatism while the PGE signatures of Group B

501     could be interpreted as BMS formed from the residue of partial melting (e.g. Guo *et al.*, 1999; Alard

502     *et al.*, 2000; Lorand & Alard, 2001; Aulbach *et al.*, 2004; Lorand & Grégoire, 2006; Powell & O'Reilly,

503     2007; Zheng *et al.*, 2007; Alard *et al.*, 2011; Saunders *et al.*, 2015; Luguet and Reisberg; 2016).

504     Group A BMS only occur between olivine crystals or at olivine-pyroxene junctions, and never as

505     inclusions inside the major silicate minerals. These textural associations are consistent with an origin

506     by melt infiltration or metasomatism inferred from the IPGE-poor and PPGE and Re-rich

507     geochemistry outlined above. However Group A BMS lack the systematic enrichment in Os over the

508     other IPGE (reflected by both $(Os/Ir)_N$ >1), and consistently lack the low Se concentrations (< 100

509     ppm), high S/Se (>3500 up to 10000) and coupled enrichment in Te and Pd that have been suggested

510     to characterise very volatile-rich metasomatism and vapour transport of Os, Pd, Au, Re and S (e.g.

511     Alard *et al.*, 2011; Delpech *et al.*, 2012). Hence, whilst the textural appearance of the sulphide

512     minerals forming Group A BMS (in addition to their interstitial setting; Table 5) would indicate a

513     metasomatic origin (e.g., Lorand & Luguet, 2016) akin to 'Type-2' BMS documented in Alard *et al.*

514     (2000). However the absence of systematic and coupled enrichment in Os, S and Pd for Group A BMS

515     suggests that these are compositionally unlike other metasomatic mantle BMS proposed to have

516     formed by vapour transport processes (e.g. Alard *et al.*, 2011; Delpech *et al.*, 2012).

517     The real paradox at Loch Roag is the origin of the Group B BMS that co-exist (with Group A BMS)

518     within each spinel lherzolite xenolith and are common in samples from at least two xenoliths

519     (samples LR80 and LR90, which were extensively documented in this study). While their trace

520     element signatures superficially resemble residual BMS, Group B are always found in spinel-feldspar

521     symplectites. Detailed petrographic studies and μCT scans clearly demonstrate that the spinel-

522 feldspar symplectites form an interconnected network throughout the peridotite (Fig. 8d-e). Further,

523 the composition of the feldspar in these symplectites (the only feldspar to occur in Loch Roag spinel

524 lherzolite xenoliths) is Na-rich ($Or_{7.6}Ab_{80.8}An_{11.6}$; Hunter & Upton, 1987; Upton *et al.*, 2011) and thus

525 not of a plagioclase composition potentially related to the break-down of spinel during

526 decompression (Rampone *et al.*, 1993; Upton *et al.*, 2011). This suggests that the feldspar in the

527 symplectites was formed during an influx of Na-rich melt or fluid. Whether this sodic-influx made use

528 of pre-existing pathways through the mantle remains unclear, but given the skeletal texture of spinel

529 (that may be crystallographically controlled e.g., Figs. 2, 4c-d, 6) and its intergrowth with feldspar, it

530 is possible that partial decompression of spinel to plagioclase may have preceded this melt influx,

531 weakening the peridotite and providing a network along which the Na-rich melt or fluid was able to

532 permeate. Additionally, as highlighted by Hughes *et al.* (2016), some Group B BMS have apatite and

533 carbonate inclusions (e.g. Fig. 6e-f; Table 5) and/or are spatially associated with 'spongy' apatite

534 crystals (themselves with carbonate and sulphide inclusions; Fig. 7). This unequivocally demonstrates

535 that the Na-rich melt or fluid responsible for feldspar formation in the symplectites was rich in $CO_2$, P

536 and S and we envisage a three-way immiscibility associated with this event.

537 Given the exclusive association of Group B BMS with the symplectites (Fig. 4c-d and Fig. 6a-b) and

538 the cross-cutting nature of these symplectite networks across the xenoliths (Fig. 8e), it is clear that

539 Group B BMS developed *after* the formation of Group A BMS. Hence the paradoxical dilemma

540 apparent within a single xenolith (*and* correspondingly noted in equivalent peridotite xenoliths from

541 Loch Roag): Group A BMS (relatively old) in many ways resemble metasomatic sulphides, yet Group

542 B BMS (relatively young) are geochemically most akin to residual IPGE-enriched BMS (e.g. Alard *et*

543 *al.*, 2000; Lorand & Luguet, 2016 and references therein). Further, the shapes and textural

544 associations observed with Group B BMS demonstrate that they formed as immiscible droplets in an

545 environment enriched in carbonate, phosphate and lithophile elements. The exact mechanism for

546 this remains unclear at this stage. Nevertheless, despite the apparently similar geochemistry, the

547    Group B sulphides at Loch Roag cannot be the same residual BMS (Type 1 BMS of Alard *et al.*, 2000)

548    as observed so often in xenoliths from other localities.

549    Further support for a non-residual origin for Group B comes from the observation of Pt-sulphide

550    (cooperite) in these BMS. The occurrence of Pt-sulphides implies that there was a high sulphur

551    fugacity ($fS_2$) associated with the formation of this group (but not such high $fS_2$ as to lead to

552    formation of pyrite, which is not observed in the Loch Roag BMS populations). More typically in

553    mantle lithologies, Pt is found in Pt-Ir-Os alloys and these are interpreted to have been formed by

554    desulphidation of Mss (as demonstrated in the experimental work of Peregoedova *et al.*, 2004 and

555    observed by Fonseca *et al.*, 2012). The partition coefficient of Pt ($D_{Pt}$) decreases with decreasing $fS_2$

556    from S-oversaturated (pyrrhotite-rich) to S-undersaturated (Fe metal-rich) conditions (Mungall *et al.*,

557    2005) and thus leads to PGE alloy nucleation. During incongruent partial melting of mantle BMS

558    (forming an initial Cu-Ni-rich sulphide liquid and a residue of Fe-Ni-rich Mss), very high PGE tenors

559    will be achieved in the residue due to high overall $D_{PGE}$, leading to saturation for Pt-Ir alloys by just

560    10% partial melting (Mungall & Brenan, 2014). No PGE alloys have been found in the Loch Roag

561    spinel lherzolite xenoliths, in either BMS group. The prevalence of Pt-sulphide in Group B BMS,

562    strictly hosted in the spinel-feldspar symplectites therefore cannot be explained by partial melting of

563    BMS and remobilisation of sulphides within this lithology (i.e., closed-system behaviour) and, in

564    accordance with inferences already made above suggests that Group B BMS were introduced during

565    a Na-rich metasomatic event that postdates formation of the Group A BMS.

566    A log $fS_2$ – T diagram was constructed from experimental and calculated stabilities of PGM in Lorand

567    & Luguet (2016) and this indicates that very specific $fS_2$ and temperature conditions are required to

568    form Pt-sulphides in mantle lithologies. For temperatures ranging 900 to 1150 °C along the olivine-

569    orthopyroxene-Mss curve (from Eggler & Lorand, 1993) $fS_2$ ranges 0.01 to 0.10. The position of Pt-

570    sulphide in Group B BMS (within chalcopyrite and/or at the edge of the BMS grains; Fig. 6c-d)

571    suggests they were exsolved during the cooling and fractionation of the sulphide droplets. Arsenic,

572   Te, Bi and Sb levels are systematically low in both groups of BMS (Table 3) indicating that semi-

573   metals were present at insufficient concentrations to scavenge Pt (or PGE in general) into a late-

574   stage semi-metal rich immiscible liquid (e.g., enriched in Te, Bi, As and Sb) to exsolve as Pt-Bi-Te-Sb-

575   As PGM (Helmy *et al.,* 2007; Holwell and McDonald 2010). The absence of Te-bearing microphases

576   and the lack of any correlation between Te and elevated Cu or Pd concentrations (c.f. Delpech *et al.*,

577   2012) further confirm the Te-poor nature of all of the Loch Roag BMS.

578   *Tellurium and gold in Loch Roag BMS*

579   The cause for the low Te in all Loch Roag BMS (in comparison to other upper mantle BMS analysed in

580   other non-cratonic studies) also remains unclear. Whilst Se and Te are not strictly coupled in their

581   chemical behaviour, they are generally seen as related chalcophile semi-metals in mantle petrology

582   (e.g., Lorand & Alard, 2010; Brenan, 2015). The partition coefficient for $D_{Te}/D_{Se}$ between Mss and

583   silicate is ~ 0.5-0.8 (Brenan, 2015). During sulphide liquid cooling and fractionation Te preferentially

584   enters the Iss portion. This could have the effect of increasing Se/Te ratio during early sulphide

585   fractionation, however we can discount this as there is no correlation (or if anything a weak anti-

586   correlation) between Te and Cu for both BMS groups (Fig. 11d).

587   By recalculating the bulk rock PGE and Au abundances of xenolith LR80 (from the analyses of a 5g

588   aliquot of powder from the unaltered core of the xenolith; Hughes *et al.*, 2014) to 100% sulphide

589   (assuming a mean sulphide abundance of 0.07% for LR80, Table 4; using the method outlined by

590   Huminicki *et al.*, 2005) and comparing this to the mean PGE and Au normalised patterns for Group A

591   and B BMS, we observe that the bulk rock PGE abundances are controlled by BMS (Fig. 12).

592   However, the bulk rock abundance of Au exceeds that present in the BMS and cannot be explained

593   by this approach (Fig. 12).

594   Recent observations of chromatographic metasomatism in mantle xenoliths from the Svalbard

595   Archipelago may provide an analogue for Au-depletion in northern European lithospheric mantle

596   (Saunders *et al.*, 2015). In the Svalbard 'Group II' and 'Group III' xenoliths, BMS (particularly 'Group

597   III-type 2 sulphides') have systematically low Au concentrations. It is suggested that these samples

598   were situated closest to a conduit in the SCLM, through which carbonate-associated melt passed,

599   resulting in the partitioning of Au into the fluid phase of this metasomatic agent and thus depletion

600   of Au in BMS in the immediate vicinity of the conduit (Saunders *et al.*, 2015). Given that we observe

601   a clear carbonate-phosphate-sulphide association in Group B BMS at Loch Roag, the low Au content

602   in these samples may similarly be an artefact of extensive equilibration with such a metasomatic

603   fluid as observed in Svalbard, but this does not explain the differing PGE abundances of the

604   *coexisting* Loch Roag BMS of Group A and B. In particular the Group B BMS are extremely PGE-rich

605   (particularly IPGE-rich) which is strikingly different from the low PGE abundance of the conduit-

606   proximal metasomatic BMS in Svalbard Group III xenoliths (Saunders *et al.*, 2015). Similarly, it may

607   not explain the depletion in Au also observed in Loch Roag Group A BMS grains (e.g., Fig. 12). We do

608   not observe a depletion in the whole-rock abundance of Au, yet a depletion in Au is apparent by *in*

609   *situ* analyses of the sulphides, consistently coupled with low Te contents for both groups of Loch

610   Roag BMS (typically 1-10 ppm Te in LR80 BMS in comparison to up to 60 ppm in Svalbard Group III

611   sulphides, Saunders *et al.*, 2015). Therefore we suggest that Au has not been stripped from the Loch

612   Roag SCLM. This 'invisible' Au could instead be hosted by a non-sulphide mineral phase, probably

613   interstitial to silicates – an idea validated by the discovery of nano-inclusions of Au in strained olivine

614   crystal margins in Pyrenean lherzolites (Ferraris & Lorand, 2014). Au readily forms telluride minerals

615   and the low Te content of the BMS may be linked to this 'invisible' Au fraction (i.e., as micro-phases

616   of Au-tellurides).


617


618   **4.2 A multi-metasomatic record of the lithospheric mantle at the margin of the North Atlantic**

619   **Craton**

The Scottish margin of the NAC became separated from the rest of the Greenlandic NAC during Palaeogene and Eocene rifting triggered by the impingement of the proto-Icelandic plume (e.g., Saunders *et al.*, 1997). The Loch Roag monchiquite dyke was intruded at 45.2 Ma (Faithfull *et al.*, 2012). Prior to this, Scotland was affected by Permo-Carboniferous rifting that led to the formation of alkaline basaltic lava flows, sills and the intrusion of a suite of lamprophyric dykes (Upton *et al.,* 2004) some of which host spinel lherzolite xenolith suites such as at Rinibar (see Fig. 1 and Hughes *et al.*, 2016). Caledonian subduction beneath the southwestern margin of the NAC in Scotland culminated in a sequence of arc-related magmatic and hydrothermal episodes (see Strachan *et al.,* 2002 and references therein) and the formation of mixed 'appinitic' (biotite-hornblende diorites) and high Ba-Sr granitoid intrusions (e.g., Fowler *et al.*, 2008). Older magmatic events of note for this region of northern Scotland include those associated with the West Highland Granite Gneiss c. 870 Ma and which probably formed as a result of crustal extension (Fowler *et al.,* 2013); Palaeoproterozoic orogenesis, arc accretion and magmatism of the Laxfordian event c. 1.67-1.90 Ga (cf. Goodenough *et al.,* 2013 and references therein, and van Gool *et al.,* 2002) equivalent to the Nagssotoqidian orogenic event in Greenland; and Palaeoproterozoic extension and rifting forming a large igneous province c. 2.4 Ga (Davies & Heaman, 2014) now represented by the Scourie Dyke Swarm in the Lewisian Gneiss Complex. Therefore, the lithospheric keel underlying the Lewisian (NAC) of Scotland has experienced a series of tectono-magmatic and metasomatic events, all or some of which may have modified its 'sulphur-budget' (Hughes *et al.*, 2016). The two BMS populations identified in the Loch Roag peridotite xenoliths likely record some of these events.

Hughes *et al.* (2015b, 2016) compared the metasomatic clinopyroxene compositions, bulk rock geochemistry, and sulphide populations across numerous Scottish mantle xenoliths. Of particular note to the present investigation was the comparison between xenolith mineralogy and geochemistry from the Loch Roag and Rinibar spinel lherzolite suites, which are entrained in Eocene and Permo-Carboniferous dykes, respectively. These two xenolith suites represent snap-shots of the lithospheric mantle composition from two different tectono-magmatic events but the occurrence of

646   Pt-sulphides in BMS associated with carbonates and phosphate is noted in both. Combined with

647   similarities in metasomatic clinopyroxene compositions, Hughes *et al.* (2015b, 2016) suggested that

648   this carbonate-phosphate-sulphide metasomatism recorded in both the Rinibar and Loch Roag

649   xenoliths must pre-date the Eocene, and probably also pre-date the Permo-Carboniferous rifting

650   that formed the Rinibar dyke.

651   If this argument is correct then it conceivably leaves the following older magmatic events as

652   responsible for formation of carbonate-associated BMS (Group B in Loch Roag) under northern

653   Scotland: (i) the Palaeoproterozoic extension event associated with the (c. 2.4 Ga) Scourie Dykes; (ii)

654   Laxfordian orogenesis (1.67-1.90 Ga); (iii) Neoproterozoic rifting associated with the break-up of

655   Rodinia (e.g., c. 870 Ma for the West Highland Granite Gneiss); and (iv) Caledonian orogenesis

656   (subduction of the Iapetus Oceanic crust in the Grampian event c. 470 Ma with Scandian continent-

657   continent collision c. 430 Ma). As detailed in Hughes *et al.* (2016), the only known carbonatite in the

658   UK occurs at Loch Urigill (near Assynt, NW Scotland) and is dated at 429.2 ± 0.5 Ma (Goodenough *et*

659   *al.*, 2011). Clinopyroxene Sr-, Nd, and Hf-isotopes from Rinibar and Streap Com'laidh spinel lherzolite

660   xenoliths have been used to infer carbonatitic metasomatism in the lithospheric mantle c. 550 ± 50

661   Ma, thought to relate to the opening of the Iapetus Ocean following the break-up of Rodinia

662   (Bonadiman *et al.*, 2008). Further, time-integrated Sr- and Nd-isotopes from Long *et al.* (1991) for

663   the Loch Roag xenolith suite (spinel lherzolites and pyroxenites) highlighted a carbonatitic

664   metasomatic event c. 2.5-2.0 Ga. Hughes *et al.* (2014) suggested that the timing of this earlier

665   carbonatite event could be related to the Scourie Dyke Swarm (c. 2.4 Ga). Carbonatite intrusions are

666   well documented in the western Greenlandic portions of the NAC by Larsen & Rex (1992) who

667   recognised five carbonatite-kimberlite-lamprophyre events: (a) c. 2.6 Ga, (b) c. 1.7-1.9 Ga (Ketilidian

668   and Nagssugtoqidian mobile belts), (c) c. 1.1-1.3 Ga (associated with the Gardar magmatic province),

669   (d) c. 600 Ma and (e) c. 169-176 Ma (Qaqarssuk carbonatite complex). Whilst the 1.7-1.9 Ga group of

670   intrusions in west Greenland do not include carbonatites, carbonatites make up a significant portion

671   of magmatic rocks in the other four events. Given the common occurrence of Pt-sulphides and

672  carbonate-phosphate immiscibility in the Rinibar spinel lherzolite xenoliths entrained during the

673  Permo-Carboniferous, it is very unlikely that the corresponding Pt-rich sulphide-carbonate-

674  phosphate Group B BMS of Loch Roag would be related to the Mesozoic Qaqarssuk carbonatitic

675  event in west Greenland. More likely, this three-way immiscibility event recorded in the Scottish

676  lithospheric mantle is related either to the c. 2.6 Ga or c. 600 Ma events recorded in the Greenlandic

677  NAC.

678  Irrespective of the exact timing of the Pt-enriched sulphide-carbonate-phosphate immiscibility event

679  that formed Group B BMS in Loch Roag spinel lherzolites, the occurrence of a PGE-rich population of

680  BMS in spinel-feldspar symplectites has important implications for the understanding of regional

681  controls on precious metal mineralisation. Hughes *et al.* (2015a) documented a temporal change in

682  Pt/Pd ratio of North Atlantic Igneous Province basaltic lavas, such that the earliest lavas were Pt-rich

683  (with a broadly chondritic Pt/Pd ratio ~ 1.8) while the youngest lavas on Iceland were comparatively

684  Pd-rich (Pt/Pd ratio ~ 0.4). Hughes *et al.* (2015a) considered it likely that this early Pt-enrichment

685  could reflect 'contamination' of ascending plume-derived magmas by lithospheric mantle BMS. This

686  is particularly the case for PGE-rich and Pt-sulphide bearing Group B BMS which are sited in positions

687  within spinel-feldspar symplectites that could be easily remobilised and assimilated by hot,

688  ascending magmas. Thus the tectono-magmatic history, as recorded by BMS for chalcophile

689  elements in the lithospheric mantle may be a useful tool towards an understanding of the inherent

690  geochemical 'fingerprints' of large igneous provinces and magmatic-hydrothermal mineralising

691  systems on a regional scale (e.g. De Wit & Thiart, 2003; Groves *et al.*, 2005; Maier & Groves, 2013;

692  Hughes *et al.*, 2016).

**5. Conclusions**

1. Detailed petrography reveals two populations of metasomatic BMS co-existing within a single mantle spinel lherzolite xenolith (LR80). By a combined approach discriminating between these populations according to BMS texture, petrographic setting, and *in situ* BMS trace element composition we can recognise these BMS groups in other spinel lherzolite xenoliths of the Loch Roag suite.

2. Given their distinct petrographic setting (i.e., interstitial to silicate grain boundaries vs. within spinel-feldspar symplectite pockets) we can infer a relative chronology of BMS groups with differing PGE and $(Re/Os)_N$ systematics:

   a. The oldest BMS (Group A) have lowest total PGE abundances and highest $(Re/Os)_N$ ratios.

   b. The youngest BMS (Group B) contain micron-scale Pt-sulphide (cooperite), have the highest total PGE abundance (particularly enriched in IPGE), lowest $(Re/Os)_N$, and are associated with a three-way immiscibility between carbonate-sulphide-phosphate.

3. Tellurium is systematically depleted in all Loch Roag BMS, and combined with discrepencies between the measured *in situ* abundance of Au in BMS and the bulk rock Au concentration, we suggest that Au-tellurides may be present as discrete interstitial phases in these mantle xenoliths.

4. Based on similarities to other mantle xenolith suites in northern Scotland (and which are hosted in older Permo-Carboniferous dykes), we suggest that the carbonatite-related event that formed Group B BMS is pre-Carboniferous.

**Figure Captions**

729 **Figure 1** – (a) Map of Scottish lithospheric terranes, as delinteated by major crustal lineaments.

730 Major mantle xenolith localities marked, and labelled for Loch Roag (LR), Rinibar (RNB) and Streap

731 Com'laidh (STP). Adapted from Upton *et al.* (2011). (b) Map of Scotland in the wider North Atlantic

732 showing cratonic correlations of the North Atlantic Craton and bounding orogenic belts

733 (Nagssugtoqidian and Ketillidian) to the north and south. Note that due to extensive

734 Palaeoproterozoic reworking the Lewisian of Scotland (north of the Great Glen Fault) is delineated as

735 'Nagssugtoqidian'.

736 **Figure 2** – (a) Hand specimen (rock slice) photograph of LR80 showing orange-green alteration halo

737 around the outer edge of the xenolith, and grey 'unaltered' core. Positions of a selection of thin

738 sections (and corresponding polished blocks) marked on. (b) and (c) show scanning electron

739 microscrope (SEM) back-scattered electron (BSE) images of some spinel-feldspar symplectites in thin

740 xenolith. Spinel is skeletal and surrounded by feldspar. Note in (c) that the wide line is a laser

741 ablation line. White arrows point to 'atoll-like' chromite within the symplectite.

742 **Figure 3** – Bulk rock geochemistry (from Hughes *et al.*, 2015). Green squares are bulk analyses of

743 various spinel lherzolite xenoliths from the Loch Roag suite. LR80 is labelled as this was the only

744 xenolith large enough to allow for the grey 'unaltered' core of the xenolith to be pulped and

745 analysed (the others incorporated some portion of green alteration halo due to their small size).

746 Crossed symbols show data from the western edge of the North Atlantic Craton in Greenland (Wittig

747 *et al.*, 2010). White-filled circle denoted primitive upper mantle (PUM) from McDonough & Sun

748 (1995). (a) Cr/Al ratio vs. Al/Si ratio. (b) Ca/Si ratio vs. Al/Si ratio. (c) Cu (anhydrous) vs. Cr/Al ratio.

749 **Figure 4** – Reflected light photomicrographs of Loch Roag spinel lherzolite xenolith base metal

750 sulphides (BMS). (a) and (b) show Group A BMS, interstitial to olivine, clinopyroxene and

751 orthopyroxene. (c) Skeletal spinel in feldspar symplectite with inclusion-bearing Group B BMS and

752  other non-inclusion bearing BMS. (d) Spinel-feldspar symplectite with finer BMS within and directly

753  adjacent to the symplectite. Note the elongate recrystallised crystals of clinopryoxene and very fine

754  BMS associated with this (right of image).

755  **Figure 5** – SEM BSE images of Group A BMS. (a) Close-up of metasomatic textures of intergrown

756  pentlandite-pyrrhotite (Pn-Po) or Mss, chalcopyrite-pentlandite (Cp-Pn), and chalcopyrite with

757  'cross-hatched' textures. (b) Similar example of metasomatic BMS textures, as in (a). (c) Pentlandite

758  (Pn) and Mss-rich (Pn-Po) example.

759  **Figure 6** - SEM BSE images of Group B BMS. (a) Spinel-feldspar symplectite with Group B BMS within

760  it. Note that line is a laser ablation line. (b) Close-up of BMS in (a) showing rounded globular texture

761  of sulphides. (c) Rounded Group B BMS with PtS (cooperite) as discrete micron-sized phase within

762  the chalcopyrite and at the margin of the BMS. Also minor galena (Ga) noted. (d) Close-up of PtS in

763  (c). (e) and (f) Inclusion-rich Group B BMS. Rounded inclusions are calcite ($CaCO_3$) whereas more

764  angular inclusions are serpentine (Serp).

765  **Figure 7** - SEM BSE images of Group B BMS associated with a discontinuous vein of apatite through

766  LR80. (a) Spongy $CaCO_3$ inclusion-rich apatite (Apt) surrounded by feldspar in vein through olivine

767  (Ol). Note rounded BMS associated with vein and patches of $CaCO_3$ outwith the apatite and

768  associated with feldspar. (b) Close-up of BMS in (a) showing rounded globular shape and inclusion of

769  apatite within BMS. (c) Close-up of spongy apatite in vein. Abundant rounded inclusions of $CaCO_3$

770  and (now) voids. Micron-scale Ni-Fe sulphide droplets labelled within spongy apatite.

771  **Figure 8** - μCT scan 3D reconstructions of portions of xenolith LR80. (a) Example of a 2D data slice (1

772  voxel in thickness) of the μCT scan of a 5mm core of LR80. A stack of these for the entire volume of

773  the xenolith was built in order to facilitate 3D reconstruction and visualisation. (b) to (c) shows a

774  sequence of frozen 3D frames of part of a slice of LR80 (approximately 2.5 cm long). The outer

775  surface of the rock scanned is shown in (b) as a semi-transparent white shell. This is gradually

776  removed by increasing transparency of the xenolith (white shell) revealing the spinel (as the higher

777  density mineral phase, along with a minor iron oxide veinlet) to be highlighted in blue in (c). (d)

778  Freeze-frame of 3D-recontructed μCT data density filtered to show spinel (in blue). Note that the

779  small density contrast between spinel and iron oxide (which occurs as a minor discontinuous veinlet

780  in one peripheral area of the scanned xenolith) means that this image includes a minor zone of iron

781  oxide (labelled on figure). (e) Same 3D dataset as (d) with showing lowest density phases (feldspar)

782  in transparent colour shells. Interconnected feldspar is shown in the same colour (i.e., the green-

783  blue shading delineates one set of interconnected feldspar, as does the brown, grey-green, pale blue

784  and red. Field of view (at front of frame) in (d) and (e) is approximately 5mm wide.

785  **Figure 9** – *In situ* major element data for BMS (from LA-ICP-MS). (a) Metal/S ratio vs. Fe/(Fe+Ni+Cu).

786  (b) Metal/S ratio vs. Ni/(Ni+Cu+Fe). (c) Metal/S ratio vs. Cu/Cu+Ni+Fe). (d) Total PGE vs. Cu. Data are

787  separated according to Group A and Group B BMS.

788  **Figure 10** - *In situ* LA-ICP-MS data for Group A and Group B BMS end member sulphide minerals (a),

789  all Group A BMS data (b) and all Group B BMS data (c).

790  **Figure 11** – *In situ* major and trace element data for BMS (from LA-ICP-MS). (a) $(Pd/Ir)_N$ vs $(Os/Ir)_N$.

791  (b) Cu vs. $(Re/Os)_N$. (c) S/Se vs. Te. (d) Te vs Cu.

792  **Figure 12** – Mass balance for bulk rock PGE and Au abundances measured in LR80 (from Hughes *et*

793  *al.*, 2014) recalculated to 100% sulphide (using the method outlined by Huminicki *et al.*, 2005) and

794  normalised to chondrite for comparison to the mean PGE and Au of normalised values of Group A

795  and Group B BMS (from LA-ICP-MS). Os is removed from this plot due to potential volatilisation of

796  this element during fire assay (for bulk rock analyses).

**Table Captions**

798 **Table 1** – Bulk rock major and trace element compositions of spinel lherzolite xenolith ('unaltered'
799 grey core) LR80 and the monchiquite dyke host to the Loch Roag xenolith suite. See Hughes *et al.*
800 (2014) for details.

801 **Table 2** – Mean BMS major element compositions for Group A and B (with and without carbonate
802 inclusions) compiled from quantitative SEM data in Supplementary Material (as a series of spot
803 analyses for each sulphide component (chalcopyrite, pentlandite and pyrrhotite, or pyrrhotite and
804 pentlandite in fine Mss intergrowths) per BMS group – i.e., Group A, B).

805 **Table 3** – Mean BMS compositions for Group A and B (with and without carbonate inclusions)
806 compiled from full LA-ICP-MS dataset in Supplementary Material (including all major elements as
807 measured by LA-ICP-MS). **S indicates that S was used for calibration of LA-ICP-MS results by
808 quantitative EDS SEM spot analyses of corresponding points. * for Ru, Rh and Pd indicates
809 abundances are reported for the element and have been corrected for isotope overlaps with argide
810 species.

811 **Table 4** – Modal abundance (by area %) of minerals in 3 thin section of LR80. See main text
812 (methods) for details of calculation.

813 **Table 5** – Group A and Group B (both carbonate and non-carbonate inclusion bearing) BMS
814 characteristics in terms of size, mineral associations and end member sulphide abundances.

815

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