Distinct sulfur saturation histories within the Palaeogene Magilligan Sill, Northern Ireland: Implications for Ni-Cu-PGE mineralisation in the North Atlantic Igneous Province

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The ~60 m thick Magilligan Sill is part of the British Palaeogene Igneous Province in the North Atlantic. The sill comprises layers of dolerite and olivine gabbro, and it intrudes a thick sequence of Mesozoic mudstones and marls, which are locally baked at the sill margins. Since 2014, the sill has been an exploration target for orthomagmatic Ni-Cu-PGE sulfide mineralisation analogous to the Noril'sk-Talnakh intrusion in Russia. We present new petrological, geochemical and S-isotope data to assess the prospectivity of the sill and the underlying magmatic plumbing system. Most sulfides in the dolerite portions of the sill are < 50 μm in size and comprise only pyrite with PGE abundances below detection limit. In the olivine gabbros, > 150 μm size pentlandite, chalcopyrite and pyrrhotite grains contain < 4 ppm total PGE, 1 460 ppm Co and 88 ppm Ag. Pyrite from the dolerites have $\delta^{34}S$ ranging from -10.0 to +3.4 ‰ and olivine gabbro sulfides range from -2.5 to -1.1 ‰, suggesting widespread crustal contamination. The S/Se ratios of sulfides in the dolerites and olivine gabbros range from 3 500 to 19 500 and from 1 970 to 3 710, respectively, indicating that the latter may have come from upstream in the magma plumbing system. The Magilligan Sill records multiple injections of mafic magma into an inflating sill package, each with distinct mechanisms towards S-saturation. Whilst the sulfide minerals in the sill do not constitute significant mineralisation themselves, detailed in-situ studies highlight a divergence in S-saturation histories, and suggest that a larger volume of olivine gabbro sulfides at depth may be prospective.

1   **Introduction**

2   Mafic-ultramafic magmatic plumbing systems in the upper crust may be highly

3   prospective for orthomagmatic sulfide mineralisation, and they host some of the largest Ni–Cu

4   and platinum group element (PGE) deposits in the world such as at Noril'sk and at Pechenga

5   in Russia (Naldrett 1997). The formation of sulfide deposits in plumbing systems requires three

6   major mechanisms: 1) The emplacement of a relatively metal-rich, initially S-undersaturated

7   mantle-derived magma from depth; 2) S-saturation of magma (normally via assimilation of

8   crustal S) and subsequent separation of immiscible sulfide from the silicate melt, followed by

9   the partitioning of chalcophile elements into the sulfide liquid; 3) Accumulation of droplets of

10   sulfide liquid forming mineralisation potentially at an economic scale (Lesher and Burnham

11   2001, Maier 2005, Maier and Groves 2011, Barnes et al. 2015). Chalcophile elements,

12   including Ni, Cu and PGE, partition strongly into sulfide phases upon the formation of an

13   immiscible sulfide liquid in a S-saturated silicate magma (e.g. Campbell and Naldrett 1979,

14   Crocket 2002, Naldrett 2004, 2010, Barnes and Lightfoot 2005). The mass ratio of silicate melt

15   interacting with sulfide liquid is described by an 'R-factor' and the mass of magma exchanging

16   siderophile metals with sulfide liquid has a strong influence on final ore composition (Campbell

17   and Naldrett 1979, Lightfoot 2007). A cumulative R-factor may be envisaged whereby

18   replenishment of a conduit system by multiple magma batches progressively upgrades the

19   sulfide tenor by allowing sulfide liquid to interact with and receive metal from large volumes

20   of silicate melt (Kerr and Leitch 2005). This process is shown to be instrumental in creating

21   conduit-hosted orthomagmatic Ni-Cu-PGE deposits such as within the Noril'sk Talnakh

22   intrusion in Russia (Barnes et al. 2016), the Platreef of the Bushveld Complex (e.g. Holwell

23   and McDonald 2007, Holwell et al. 2011, Ihlenfeld and Keays 2011), the Insizwa Complex of

24   South Africa (Lightfoot et al. 1984), and Voisey's Bay in Canada (Huminicki et al. 2008).

25   A silicate melt can dissolve sulfur until it reaches the threshold of sulfur content at

26   sulfide saturation (SCSS; Shima and Naldrett 1975). Adding excess crustal sulfur via

27   assimilation may cause a magma to exceed the SCSS, and melting of country rock sulfides can

28   directly introduce a sulfide xenomelt into the magma (Lesher 2017). Changing the pressure,

29   temperature, and/or oxidation state of the magma can also shift the SCSS. In either case this

30   forces the magma to exsolve an immiscible sulfide liquid (Mavrogenes and O'Neill 1999). The

31   S-isotopic composition of sulfide minerals (e.g., $\delta^{34}S$) in high degree mantle melts is near

32   chondritic, while sulfides in crustal rocks are more isotopically variable (Faure 1977). Mantle

33    $\delta^{34}S$ is typically 0.1 ± 0.5 ‰ (Sakai et al. 1984), and values different from this indicate

34   assimilation of crustal rock in a magma. A second tool for analysing the causes for sulfide

35   saturation is the S/Se ratio of sulfides. Contrasts in S/Se are often much larger and more

36   sensitive than $\delta^{34}S$. In the absence of crustal contamination, sulfides in mantle-derived magmas

37   will have S/Se < 4,000 (Lorand et al. 2003, Lorand and Alard 2010) with typical 'mantle-like'

38   S/Se ratios ranging from 2 850 to 4 350 (Eckstrand and Hulbert 1987). Divergence from the

39   average mantle ranges of $\delta^{34}S$ and S/Se indicates contamination of the magma by crustal sulfur

40   or partial oxidation of the sulfide minerals after crystallisation. Sulfur-saturation can occur

41   multiple times and at different depths in conduit systems (e.g. Li et al. 2009, Hayes et al. 2015),

42   and thus studies using geochemical proxies and indicators for the causes of S-saturation must

43   take this into account. Hence, a combination of $\delta^{34}S$ and S/Se can be used to produce a more

44   complete picture of the triggers for S-saturation (including R-factor; Lesher and Burnham

45   2001) and as an exploration vectoring tool towards mineralisation in orthomagmatic systems

46   (Queffurus and Barnes 2015, Smith et al. 2016).

47   Platinum-group minerals (PGM) and small-scale sulfide mineralisation is documented

48   on the Isles of Skye, Mull and Rum (Butcher et al., 1999; Pirrie et al., 2000; Power et al., 2000,

49   as reviewed by Hughes, 2015) in the Scottish portion of the British Palaeogene Igneous

50   Province (BPIP). The region is part of the North Atlantic Igneous Province (NAIP), an area

51   that has been highlighted as potentially prospective for orthomagmatic PGE mineralisation

52   (Andersen et al., 2002). Recent studies on the islands of Skye and Rum have also highlighted

53   extensive contamination of shallow Palaeogene intrusions by crustal S from Mesozoic

54   sediments (Power et al. 2003, Hughes et al. 2015a, 2016), exemplified by light S-isotopic

55   compositions of steeply dipping conduits (e.g. Hughes et al. 2015). By comparison, little

56   research has been carried out on orthomagmatic mineralisation and S sources in the Irish

57   portion of the BPIP.

58   The Magilligan Sill is a mafic intrusion on the north coast of County Londonderry,

59   Northern Ireland. It crops out close to the western edge of the Antrim Plateau, and is part of

60   the BPIP. While the Magilligan Sill has never been dated, ^{40}Ar–^{39}Ar geochronology for the

61   nearby Portrush Sill estimates an age of 54.9 ± 0.6 Ma (McKenna 2009). We speculate that the

62   two sills are of comparable ages given their lithological similarity and their emplacement

63   beneath the Antrim lavas and into Mesozoic sediments. Given its setting within a large igneous

64   province, injected through a thick sequence of S-rich crustal sediments, the Magilligan Sill

65   became an exploration target for Lonmin (Northern Ireland) Ltd, who investigated the site from

66   2014 to 2017. This paper presents the first detailed account of the petrology and geochemistry

67   of the Magilligan Sill. We use sulfide-specific and bulk rock S-isotope compositions together

68   with *in situ* sulfide major and trace element analyses of Lonmin borehole core samples from

69   the sill to establish the causes of S-saturation in magma batches prior to emplacement into the

70   intrusion. We use this to assess the prospectivity of the sill itself as well as that of the

71   surrounding magmatic plumbing system, using Noril'sk as an analogue.

72   **Regional Geology**

5

73   The North Atlantic Igneous Province formed during a period of continental flood basalt

74   magmatism as the proto-Icelandic mantle plume impinged upon the thick continental

75   lithosphere under the North Atlantic and Rae Cratons, and adjoining orogenic belts.

76   Continental flood basalt magmatism (both tholeiitic and alkalic) initiated c. 62 Ma across what

77   is now Greenland and Baffin Island, and the UK and Ireland (in the form of the BPIP), and

78   associated rifting ultimately led to the opening of the Atlantic Ocean (Saunders et al. 1997).

79   BPIP lavas were erupted over a timespan of approximately 3 Myr (61-58 Ma; White and Lovell

80   1997). Several volcanic disconformities within the now eroded lava fields (Single and Jerram

81   2004) juxtapose lava batches that were fed by multiple volcanic centres or fissure systems

82   (Jerram and Widdowson 2005).

83   *Palaeogene lavas*

84   In Northern Ireland, the geology of County Antrim and the eastern edge of County

85   Londonderry is dominated by onshore lava fields of the BPIP. Along with the Isles of Skye and

86   Mull in Scotland, Antrim hosts some of the best-preserved examples of Palaeogene flood

87   basalts in the North Atlantic region (Wilson 1972, Kerr 1997). The Antrim Plateau lavas cover

88   roughly 3 800 km^2 and are stratigraphically separated into the tholeiitic Lower and Upper

89   Basalt Formations (Lyle and Patton 1989) – Figure 1. The up to 531 m thick Lower Basalts

90   were erupted at 62.6 ± 0.6 Ma (Ganerød et al. 2011). They become more intermediate in

91   composition up-sequence (Lyle and Patton 1989), including isolated interbasaltic rhyolite

92   extrusions in the Tardree Mountains in the centre of the Lower Basalts (Ganerød et al. 2011).

93   The up to 346 m thick Upper Basalts were erupted at 59.6 ± 0.6 Ma and they mark a return to

94   more primitive compositions (Ganerød et al. 2011).

95   The thickest and most extensive lava field in the Scottish portion of the BPIP on the

96   Isle of Mull is estimated to be 1800 m thick, covering approximately 840 km^2 (Emeleus and

6

97   Bell, 2005). In contrast to the Antrim lavas, the Mull Lavas have been divided into three

98   principal groups (in chronological order; the transitional tholeiitic-alkalic Mull Plateau Group,

99   the Coire Gorm type lavas, and the Central Mull Tholeiites) according to the petrogenetic and

100   geochemical characterisation of Kerr (1993, 1995). For the Antrim lavas, it has been postulated

101   that the reappearance of tholeiitic mafic magma was the product of a later, more extensive

102   melting event within the proto-Icelandic plume source (Lyle 1985, 1988). However, a more

103   recent interpretation of the changing magmatic regime of the plume, as represented by the Mull

104   lavas, was proposed by Kerr (1993, 1995) and Kerr et al. (1999) who identified a change from

105   small degrees of partial melting of a deeper, garnet-bearing mantle source to progressively

106   higher degrees of partial melting of a shallower and depleted spinel-bearing mantle.

107   *Palaeogene magma plumbing systems*

108   Palaeogene igneous intrusions are emplaced into most levels of the Mesozoic

109   stratigraphy in Northern Ireland. NW-SE trending dyke swarms detected by magnetic surveys

110   occur under much of the Antrim Plateau (GSNI 2004), and are analogous to those observed in

111   the Scottish portions of the BPIP. Dolerite sills intrude Mesozoic sedimentary rocks exposed

112   along the north Antrim coast, including the Portrush and Magilligan Sills (Wilson 1972) (Fig.

113   1). The Portrush Sill is the more studied of these two intrusions, with work published on its

114   petrology and country rock contact metamorphism (Ledevin et al. 2012). The Portrush Sill

115   comprises a highly altered olivine gabbro with thin aphanitic chilled margins. As the sill

116   intruded, it baked the surrounding Jurassic siltstones to cordierite hornfels facies for ~10 m

117   from the intrusion margins (Ledevin *et al*., 2012). It is younger than the Antrim Plateau Lavas

118   (54.9 ± 0.6 Ma; McKenna, 2009), consists of a main sill with two smaller sills above it, and is

119   estimated to be 45-60 m thick. Unlike intrusions at Noril'sk or Pechenga, the Portrush Sill is

120   thought not to have fed a large volume of magma to the surface.

121   The Magilligan Sill (Fig. 1, 2), first documented in the subsurface via drilling during a

122   Mineral Reconnaissance Programme drilling campaign (BGS 1964), has rarely been mentioned

123   in the literature. Wilson (1983) describes it as a ~60 m thick dolerite sill emplaced into Jurassic

124   Lias mudstones, which are underlain by Triassic and Permian sediments (Fig. 2). There is no

125   published geochronological or geochemical data available for the sill.

126   By contrast, there is an abundance of published literature on the petrology and

127   magmatic development of the Trotternish Sills and Shiant Sill (Fig. 1) of the Isle of Skye and

128   Shiant Isles, respectively (Scottish BPIP). Like the Magilligan and Portrush Sills, the

129   Trotternish Sills and Shiant Sill are not contemporaneous with the adjoining lava field (Skye

130   lava field). The Trotternish Sills are 250 m thick, comprising individual sub-alkaline intrusions,

131   up to 130 m thick (Gibson 1990). The sills contain 'fingers' or horizons of picrites,

132   picrodolerites and crinanites, many of which have chilled margins (Gibson and Jones 1991).

133   The Shiant Sill lies further west and is more alkaline than the Trotternish Sills, but is similar in

134   thickness and also contains multiple intrusive units (Gibson and Jones 1991). The Shiant Sill

135   is dominated by crinanites and picrodolerites with infrequent metre-thick picrite horizons (Gibb

136   and Henderson 1984). The sills in both localities are thought to have formed from discrete

137   pulses of differentiating alkali-basalt magma being injected into the sill from a single,

138   chemically zoned chamber beneath the sill complex (Gibson and Jones 1991). The geology of

139   the Magilligan, Portrush and Trotternish Sills is compared in Figure 3.

140   ***Mesozoic sedimentary basin***

141   The Palaeogene intrusions were emplaced into sedimentary rocks of the British

142   Hebridean basin and as such, the country rocks are similar in both Northern Ireland and

143   Scotland. The Magilligan and Portrush Sills in Northern Ireland intrude the Lower Jurassic

144   Waterloo Mudstone Formation of the Lower Lias Group (GSNI 2004), whereas the Trotternish

145   Sill intrudes the Middle Jurassic Lealt Shale and Valtos Sandstone Formations of the Great

146   Estuarine Group (Woodcock and Strachan 2012) (Fig. 3). The Shiant Sill intrudes Lower Lias

147   Group sediments, a large raft of which separates the intrusion into two bodies that were

148   previously thought to be distinct (Gibb and Henderson 1984). Intermittent evaporite horizons

149   are common within the Mesozoic northern British basin (GSNI 2004). The entire Mesozoic

150   succession in Britain represents a S-rich source that could have contaminated and assimilated

151   Palaeogene intrusions.

152   **Geology of the Magilligan Sill**

153   The Magilligan Sill has a chilled upper margin of aphyric to very fine-grained, normally

154   olivine-deficient dolerite, present in all exploration boreholes, below which is a 5 m thick zone

155   of vesicular fine-grained dolerite (Fig. 4). The sill coarsens gradually to become a gabbro 10-

156   20 m from the intrusion margin, with rare olivine identified in the majority of the drill core.

157   Green-tinged (more olivine-rich), 1-5 m thick layers, that are distinct from the dark grey

158   gabbros, occur sporadically throughout the sill. Within the bottom 10 m of the sill, the grain

159   size decreases progressively to form a lower chilled dolerite margin with abundant vesicles in

160   the lowermost 1-2 m. Rafts of baked sediment occur within the intrusion, and < 1 m isolated

161   zones of dolerite occur within the country rock outside the main intrusion. Multiple layers of

162   dolerite/gabbro form individual units in the intrusive sequence (Fig. 4). Each unit coarsens

163   downwards and displays a range of crystal sizes across their thickness, but overall the centre

164   of the sill is significantly coarser than the margins. The country rock surrounding the sill

165   comprises mudstone with occasional phosphatic and sandy units, and is notably baked and

166   metamorphosed to hornfels in the 1-3 m immediately next to the sill contact. Outwith the baked

167   contacts, the mudstones are dark grey, fissile and pyrite-rich. Proximal to the sill, baked

168   mudstones are very fine grained, cordierite facies slates with visible fine pyrite.

169   **Methodology**

170   A total of forty-seven half or quarter diamond drill core samples were collected for this

171   study from three Lonmin boreholes that intersect the sill and the overlying and underlying

172   Mesozoic sedimentary rocks. These boreholes are referred to here as "Boreholes 1, 2 and 3",

173   and their locations are shown in Figure 2. Table A1 (see Supplementary Material) gives a full

174   list of hand specimen descriptions for all drill core samples.

175   *Microscopy and mineral analysis*

176   Transmitted and reflected light optical microscopy was undertaken at Camborne School

177   of Mines (CSM), University of Exeter, using a Nikon Eclipse E600 Pol microscope with Nikon

178   Digital Sight 5MP camera on 12 polished thin sections prepared from the Magilligan Sill drill

179   core samples and its country rocks.

180   Quantitative mineral analysis was undertaken on eight of the polished thin sections of

181   the sill samples at CSM with a JEOL JXA-8200 Electron Microprobe (EPMA), using a

182   Wavelength Dispersive Spectrometer (WDS). Silicate and sulfide standards were used to

183   calibrate for major elements Si, Na, Cr, K, Al, Mg, Mn, Ca, Fe, Ni, Zn, Ti and V, and Fe, S,

184   Ni, Pb, Co and Cu, respectively. Standard analyses and results are shown in Table S1 (silicates

185   and sulfides) (see Supplementary Material). The beam parameters were 15 nÅ, at 15 kV for

186   thin section samples 1, 5, 6 and 7, and 1 nA at 20 kV for thin section samples 2, 3, 8, and 10.

187   Major elements (Si, Na, K, Al, Mg, Mn, Ca, Fe, S) had counting times of 20 s peak and 10 s

188   background, while minor/trace elements (Cr, Ni, Zn, Ti, V, Pb, Co, Cu) were 30 s peak and 15

189   s background. Backscattered electron images were taken separately using the same instrument.

190   *LA-ICP-MS*

191   Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was

192   undertaken at the School of Earth and Ocean Sciences, Cardiff University, on polished thin

193   sections using a New Wave Research UP213 UV laser system with a Thermo X Series 2 ICP-

194   MS. Laser analyses were utilised in order to investigate the trace element content of individual

195   sulfide grains *in situ* within samples, with the beam moving across mineral surfaces linearly.

196   The beam size was 40 μm, using a 10 Hz current with a power of ~6 Jcm^{-2} and an average

197   ablation rate of 6 μms^{-1} along a programmed linear route. Acquisition times ranged from 70 to

198   150 s, with longer times for larger sulfides (according to laser line length), with an additional

199   40 s per acquisition to accommodate gas blank measurement and chamber flushing/evacuation.

200   Calibration was conducted using three in-house sulfide standards of known compositions

201   developed at Cardiff University (for further details see Prichard et al. 2013, Smith et al. 2014).

202   Major elements ^{57}Fe, ^{61}Ni and ^{65}Cu, and trace elements ^{59}Co, ^{66}Zn, ^{75}As, ^{77}Se, ^{95}Mo, $^{99,\ 101}$Ru,

203   ^{103}Rh, $^{105,\ 106,\ 108}$Pd, ^{109}Ag, ^{111}Cd, ^{121}Sb, ^{125}Te, ^{185}Re, ^{189}Os, ^{193}Ir, ^{195}Pt, ^{197}Au, ^{206}Pb and ^{209}Bi

204   were calibrated using these standards. Sulfur concentrations were assumed based on sulfide

205   mineralogy. Following calibration, the Memorial Pyrrhotite Po724 standard was run as an

206   unknown to check machine accuracy. An internal pyrite standard was analysed as a qualitative

207   comparison for stoichiometric S values of pyrite, pyrrhotite, pentlandite and chalcopyrite. The

208   results of each stage of calibration are shown in Table S2 (see Supplementary Material).

209   ***Sulfur isotopes***

210   Sulfur isotope analyses were undertaken at the Scottish Universities Environmental

211   Research Centre (SUERC), University of Glasgow. A representative subset of six sill samples

212   and five sediment samples were selected for conventional sulfur isotope analysis. Individual

213   sulfide crystals were handpicked from within sedimentary samples for analysis. Sill samples

214   were crushed using a standard jaw crusher, sieved and manually ground into a powder, with as

215   little silicate material as possible. 5 mg of each powdered sample was added to 200 mg of CuO

216   powder (for a single analysis) and the compound was homogenised using a mortar and pestle,

217   and stored in a glass pellet. For sill samples, due to the small sulfide size, a Frantz Magnetic

218 Barrier Lab Separator was used to separate most of the silicate minerals, retaining the sulfides

219 (mainly the paramagnetic pyrrhotite) for blending with the CuO powder. The compound

220 samples were then combusted in their glass pellets at 1020 °C, and the gas emitted was

221 extracted into a vacuum line. Water was frozen off in acetone and dry ice, and SO_2 and CO_2

222 were separated by a multistage freeze-thaw system using liquid nitrogen and N-pentane. SO_2

223 was collected at the end of the process, and detected by a ThermoFisher Scientific MAT 253

224 dual inlet mass spectrometer. The spectrometer measures the abundance of ^{34}S and ^{32}S in the

225 gas, giving a relative ratio of the two isotopes ($\delta^{34}S$). The ratio was compared to an in-house

226 SO_2 gas standard of known $\delta^{34}S$. The raw $\delta^{34}S$ was then calibrated using the Vienna Canyon

227 Diablo Troilite (VCDT) global $\delta^{34}S$ standard for sulfur isotope analysis, and results reported in

228 ‰ relative to the VCDT. Multiple runs of two powdered international standards (chalcopyrite

229 CP-1, -4.56 ‰; sphalerite NBS-123, +17.1 ‰) and one in-house standard (silver sulfide IAEA-

230 S-3, -32.2 ‰) were analysed using the conventional sulfur gas extraction line as unknowns

231 prior to sample analysis to test calibration accuracy. Standard analyses were repeated twice to

232 establish data precision. Standard calibration results and sample repeats are shown in Table S3

233 (see Supplementary Material).

234 **Results**

235 *Petrology*

236 The locations of thin section samples T1-12 with respect to Boreholes 1-3 are shown in

237 Figure 4. Dolerites at the topmost sill contact (e.g., T1, 4, 5 and 6) generally have a very fine-

238 grained almost aphanitic groundmass (<100 μm), and are primarily composed of subophitic

239 semi-chloritized augite and anorthite (highly altered to zeolites and clays), with infrequent

240 olivine phenocrysts (completely or partially serpentinised or chloritized). Dolerites below this

241 ~2 m chilled margin contain 200 to 700 μm diameter zeolite-quartz-calcite-filled vesicles over

242   a depth interval of approximately 5 m. The lowermost contact of the sill (T10 and 12) is

243   texturally and mineralogically similar to the top one, with a 1 m thick chilled margin and a 3

244   m thick vesicular zone. Augite, anorthite and altered olivine phenocrysts dominate the very

245   fine-grained groundmass. Chlorite is abundant, not only partially replacing mafic minerals but

246   also appearing interstitially, in fractures, and as part of the matrix. In the top and lower sill

247   contacts, small spinels (<500 μm and ranging titanomagnetite to ilmenite) make up >5% of the

248   rock.

249   Inwards from the contact zones, the sills become coarser (mm-scale crystals) and thus

250   are classed as gabbros. However, individual segments of the sill package vary considerably in

251   their mineralogy – for example, T2 and 3 of Borehole 3 are simply coarser versions of the rocks

252   found at the top contact of the sill (gabbros), whereas T7 and 8 of Borehole 1 are distinct with

253   a notably higher olivine content (olivine gabbros). The olivine gabbros in the core (observed

254   in mainly in Borehole 1, with sub-metre thick sections in Borehole 3) have their own chilled

255   margins (10-20 cm thick) and glassier olivine crystals at the edge. In general, clinopyroxene

256   and plagioclase are the major components of all gabbros (40-50 % and 25-40 % respectively).

257   Olivine gabbros contain >30 % olivine, which is reasonably fresh and with minor iddingsite

258   within fractures (Fig. 5a). Olivine found in gabbros (5-10 % of their composition) is always

259   serpentinised (Fig. 5b). Orthopyroxene occurs in T2 only with an abundance of < 5 %. As seen

260   in the chilled margins, spinels in the central portions of the sill are an intricate mix of

261   titanomagnetite and ilmenite (and equigranular with surrounding groundmass silicates, on a

262   millimetre-scale).

263   Sulfide minerals are observed with variable abundances throughout all units and

264   lithologies in the sill. The upper and lower contact zones and the coarser gabbro sections of the

265   sill host trace (<1 %) interstitial small grains (averaging ~50 μm) of pyrite and pyrrhotite only

266   (Fig. 5c). Chalcopyrite and bornite (<70 μm) are found in very rare instances. By contrast, the

13

267 olivine gabbro units contain a mixture of sulfides (generally >150 μm) in higher proportions

268 (1-2 %) including pyrite, pyrrhotite, chalcopyrite, pentlandite, and galena – normally in

269 complex intergrowths (Fig. 5d). Sulfides in the olivine gabbros are often partially oxidised

270 (10-20 % around rims) with skeletal grain shapes due to dissolution. In comparison, sulfides in

271 the gabbros are generally fresher (< 5 % surface alteration). No platinum group minerals (PGM)

272 are observed in the samples.

273   ***Mineral chemistry***

274   *Silicates*

275   The major element compositions of clinopyroxenes in the sill are distinct between

276 gabbros and olivine gabbros (Fig. 6a-b) – the olivine gabbros contain magnesian and/or calcic

277 pyroxenes (14.0-15.5 wt. % MgO, 22.0-22.5 wt. % CaO and 5-7 wt. % FeO), whereas all other

278 pyroxenes are more iron-rich (7-11 wt. % FeO, with 12-14 wt. % MgO and 20.5-22.0 wt. %

279 CaO). As such, olivine gabbro clinopyroxenes are less augitic, with Mg, Ca, Fe, and Al bearing

280 varieties found in T7 and 8. Individual pyroxenes in the olivine gabbros are often

281 compositionally zoned. Olivine in olivine gabbros have Fo% of ~65 compared to ~50 in

282 (unserpentinised) olivine in other sill lithologies. Plagioclase is systematically more anorthitic

283 in olivine gabbros with mean An% of 82, compared to 70 in the gabbros. A full list of major

284 element concentrations can be found in Supplementary Table S4.

285   *Sulfides*

286   A summary of major and trace element compositions of sulfides from the Magilligan

287 Sill and surrounding country rocks obtained from LA-ICP-MS are presented in Table 1, with

288 the full list displayed in Supplementary Material Table S2. Figures 7a-d summarise the trace

289 element geochemistry of sulfides found in the Magilligan Sill. Cobalt is concentrated in olivine

290 gabbro sulfides, with the highest amounts (< 2 700 ppm) found in pentlandite; the average Co

14

291 concentration across all olivine gabbro sulfides above detection is 1 460 ppm. Silver is present

292 between 2.3 and 315 ppm in olivine gabbro sulfides (highest in pentlandite, although also

293 present in chalcopyrite), with an average of 88 ppm across all olivine gabbro sulfides above

294 detection. Sulfides excluding those in the olivine gabbros contain < 0.12 ppm Re, < 570 ppm

295 Co and < 5.3 ppm Ag. Figures 7a and 7b show a slight positive correlation between Ni

296 concentrations and Co/Ag concentrations in sulfides. The PGE are below detection in pyrite

297 from dolerites (from the upper and lower contact zones) and gabbros throughout the sill

298 package. By contrast, sulfides in the olivine gabbros contain up to 4 ppm total palladium-group

299 PGE (PPGE; Rh, Pt and Pd), and up to 0.24 ppm iridium-group PGE (IPGE; Os, Ir and Ru). In

300 T7 and 8, Ru and Rh are only found in chalcopyrite grains (average of 0.2 and 0.65 ppm,

301 respectively). The remaining PGE are found in both chalcopyrite and pentlandite (Fig. 7c-d):

302 Pd is more abundant in chalcopyrite (0.25 – 2.43 ppm); Pt is more abundant in pentlandite (0.03

303 – 0.66 ppm); and Os and Ir have been recorded close to background in both minerals between

304 0.02 and 0.05 ppm. Rhenium is also more abundant in olivine gabbro chalcopyrite and

305 pentlandite than pyrite from other gabbros and dolerites (0.04 – 0.96 ppm compared to a

306 maximum of 0.12 ppm, respectively). The absence of visible PGM suggests that PGE are found

307 within sulfide structures.

308 Selenium concentrations for Magilligan sulfides are plotted against Ni and total PGE

309 concentrations (from Table S2, Supplementary Material) in Figures 8a-c. Olivine gabbro

310 sulfides have Se concentrations between 91 and 171 ppm, with S/Se ratios between 1 980 and

311 3 720. Sulfides in the remainder of the sill have Se concentrations between 21 and 95 ppm (if

312 above the detection limit), and S/Se ratios ranging from 3 510 to 25 200. Sulfides in the local

313 sediment have Se concentrations between 49 and 99 ppm, and S/Se ratios of between 5 390

314 and 10 800. In a comparison between S/Se and total PGE concentrations (Fig. 8c),

315 chalcopyrites in the olivine gabbros tend to have S/Se ratios of 1 980 – 3 340 and total PGE

316   concentrations of 0.6 – 3.7 ppm. Pyrrhotites and pentlandites are similar in terms of S/Se (~ 2

317   700–3 700), but pentlandite tends to have higher total PGE (< 2.5 ppm). The absence of the

318   highest S/Se values in Fig. 8a-c reinforces the fact that sulfides with high S/Se (e.g. gabbros,

319   marginal dolerites and sediment) have, in almost all cases, no detectable PGE or Ni.

320   ***Sulfur isotope compositions***

321   A summary of $\delta^{34}S$ compositions for the Magilligan Sill and surrounding country rock

322   is shown in Table 2 (full dataset in Supplementary Table S3) and Figure 9a. Mesozoic shales

323   adjacent to the sill have $\delta^{34}S$ values ranging from -10 to +5.3 ‰ above the intrusion and from

324   -20.4 to -14.9 ‰ below it. Dolerites at the intrusion edge have $\delta^{34}S$ values between -9.6 and -

325   2.5 ‰, whereas gabbros are consistently +3.4 ‰. Olivine gabbros have $\delta^{34}S$ values from -2.5

326   to -1.1 ‰.

327   Combined $\delta^{34}S$ and S/Se data (from the LA-ICP-MS dataset) are displayed in Figure

328   9b. S/Se and $\delta^{34}S$ values of the sill and its surroundings can be compared to the magmatic norm

329   for each parameter. Only olivine gabbro samples overlap the 'magmatic' boundaries of S/Se (2

330   850-4 350; Eckstrand and Hulbert 1987, Queffurus and Barnes 2015) and $\delta^{34}S$ (0.1 ± 0.5 ‰;

331   Sakai et al. 1984), highlighted by the hatched square in Figure 9b. S/Se values for the olivine

332   gabbros and sediments are more restricted compared to the wide ranges observed in the

333   dolerites and gabbros. In general, sulfides in the dolerites and gabbros have S/Se ratios 2-5

334   times that of the maximum magmatic norm (up to 20 000 compared to less than ~4 000). Figure

335   10 presents a downhole log of the Magilligan Sill in terms of S/Se ratios, S isotopes and trace

336   element concentrations in sulfides. High PGE, Ni, Cu and Ag contents are confined to the

337   olivine gabbro sulfides only, and S/Se and $\delta^{34}S$ downhole trends appear to mirror each other.

338   **Discussion**

339   ***Magmatic history of the Magilligan Sill***

16

340   The Magilligan Sill has a coarse gabbroic interior and chilled doleritic margins, fitting

341   well with descriptions of similar sills found within the BPIP – the Portrush Sill, of a similar

342   thickness and mafic petrology (Ledevin et al. 2012); and the thicker Trotternish Sills, with

343   distinct chemical changes throughout (Gibson 1990, Gibson and Jones 1991). As the magma

344   intruded the Mesozoic Waterloo mudstones (Fig. 11a), the outermost parts of the sill would

345   have cooled rapidly, resulting in the very fine-grained and vesicular dolerites seen in T1, 4, 5

346   and 6 (top), and T10 and 12 (bottom). Heat transfer from the sill would have simultaneously

347   metamorphosed country sediment to cordierite hornfels facies (Fig. 11b), in a similar fashion

348   to the Portrush Sill (Ledevin et al. 2012). Following intrusion, water from an external source,

349   potentially meteoric, altered olivine and plagioclase in the crystallised sill to produce hydrous

350   silicates (Fig. 11c). The inwards gradation to coarser grained rocks (T2 and 3) is observed in

351   all three boreholes, which contain similarly altered augite, anorthite, and titanomagnetite-

352   dominated compositions in all but the olivine gabbro samples that occur sporadically

353   throughout the sill. These olivine-rich portions (e.g. T7 and 8) feature large, reasonably fresh

354   olivine crystals, and are chemically and texturally distinct from the rocks found elsewhere in

355   the sill. Their pyroxenes are Mg- and Ca-rich as opposed to Fe-rich, their plagioclases are more

356   anorthitic than albitic, and they are less pervasively altered. The abrupt nature of the marked

357   downhole petrological changes from dolerite/gabbro to olivine gabbro indicates that the

358   variation is not gradational, and the presence of fine, glassy margins within olivine gabbro

359   sections implies that they were chilled against already solidified and cooled dolerites and

360   gabbros. Hence, we conclude that the olivine gabbros are formed from new pulses of primitive

361   magma emplaced into the earlier and already altered gabbro-dolerite sill to form distinct

362   olivine-rich horizons observed in the sill (Fig. 11d).

363   In the Magilligan Sill, the clinopyroxene-plagioclase dominated rocks are more altered

364   and superseded by fresher modal olivine melts, inconsistent with Bowen's discontinuous

365   reaction series, in which high temperature olivine crystallisation normally precedes

366   clinopyroxene and plagioclase crystallisation in a cooling system (Bowen 1979). The more

367   forsterititc olivine and anorthitic plagioclase in the olivine gabbros also suggest higher

368   temperature crystallisation. We suggest that the magmatic system was replenished by younger,

369   more primitive mantle melts following the initial emplacement of gabbros and dolerites, or that

370   the olivine-rich horizons were formed from a completely different magma. It is unlikely that

371   the entire magma source changed, given the localised nature of the sill, and thus re-introduction

372   of mafic melts into a deeper magma reservoir is the preferred scenario.

373   We envisage that the Magilligan Sill developed in a similar manner to the Trotternish

374   Sills. A stepwise decrease in MgO content throughout the petrological units of the Trotternish

375   Sills from oldest to youngest (40 % in picrites, 20-10 % in picrodolerites, and 5 % in crinanites)

376   reflects an evolving magma system with each unit injected in discontinuous pulses (Gibson

377   1990). The Skye lava field ranges in composition from basalt and picrobasalt to hawaiite and

378   mugearite, also suggesting a differentiating source during Palaeogene volcanism (Hughes et al.

379   2015b). Internal chilled margins within the Trotternish Sills and Shiant Sill reinforce the idea

380   of multiple injections – these are also present within the Magilligan Sill. If a magma chamber

381   were replenished between units, subsequent magma compositions would be more mafic than

382   the previous one (provided the influx is volumetrically significant relative to the resident

383   magma). This is observed in the increasingly mafic, late-stage Mull lavas (Kerr 1997). The

384   presence of multiple magma injections within equivalent sills across the BPIP and the presence

385   of olivine in the centre of the Magilligan Sill suggests that they are formed by similar petrogenic

386   processes. The Antrim Plateau Lavas and the Magilligan Sill follow similar evolutionary trends

387   towards mafic (magnesian) compositions from Lower to Upper Basalts, and from gabbro to

388   olivine gabbro, respectively.

389   ***S-saturation and the formation of sulfides***

18

390   Magmatic sulfides typically have δ^{34}S values of 0.1 ± 0.5 ‰ (Sakai et al. 1984). Some

391   modern studies of MORB lava sulfides suggest larger ranges (Eckardt 2001, Seal 2006, Labidi

392   et al. 2012), but the original values presented by Sakai *et al* account for seafloor sulfate/sulfide

393   fractionation and are thus more precise and reliable (Lesher 2017). The local pristine magmatic

394   δ^{34}S signature of the Scottish BPIP has been found to be −2.3 ± 1.5 ‰ (Hughes et al. 2015a)

395   based on the mean composition of the picritic Trotternish Sills (Hughes et al. 2015a), which is

396   comparable with that of Icelandic basalts (Torssander 1989) and MORB (Labidi et al. 2012).

397   The Magilligan Sill sulfides record values between -9.6 and -1.1 ‰, and one sample (T2) has

398   +3.4 ‰. Sulfides in local sediments adjacent to the sill record average δ^{34}S values of -6.0 ‰

399   (above the sill) and -17.7 ‰ (below the sill). It follows that most of the sill magmas have

400   experienced some degree of crustal contamination, as the addition of isotopically light crustal

401   sulfur from the Mesozoic country rocks will shift their primary magmatic sulfide signature

402   (assumed to be -2.3 ‰ for the BPIP; Hughes *et al.*, 2015). Based on work on the Trotternish

403   Sills (Hughes et al. 2015a), the proportion of sedimentary sulfur assimilated by the magma (f)

404   can be calculated, using the observed δ^{34}S values achieved in the contaminated sill (δ^{34}S$_{mix}$)

405   using the following equation:

406   $$\delta^{34}S_{mix} = \frac{\delta^{34}S_c X_{cf} + \delta^{34}S_m X_m (1-f)}{X_{cf} + X_m (1-f)}$$

407   Here, δ^{34}S$_m$ and δ^{34}S$_c$ are the S isotopic conditions of the uncontaminated magma (0

408   ‰) and the local sediment, respectively (-20.4 to -9.9 ‰). X_m and X_c are the concentrations of

409   S in the magma and sediment, respectively. Figure 12 shows a binary mixing model between

410   the sill and sedimentary sulfur, based on the calculation above. The upper margin of the sill

411   contains around 8 % sedimentary sulfur, whereas the lower margin contains only 1 %. Around

412   0.8 % of the sulfur in the olivine gabbro samples comes from sedimentary sulfur, and the

413   gabbro samples contain almost no sedimentary sulfur (0.05 %). It follows that the margins of

414   the intrusion will have had a greater degree of crustal interaction and S assimilation. The

19

415   diffusion of volatiles at the margins of the hot intrusion could have promoted the transfer of S

416   both from and into the proximal sediment (Penniston-Dorland et al. 2008), while direct

417   assimilation of crust would provide larger abundances of S more rapidly (Robertson et al.

418   2015). Marginal dolerite $\delta^{34}S$ deviates strongly from 'mantle-like' values (Sakai et al. 1984).

419   Despite being the only positive magmatic sample, gabbro sample T2 appears too isotopically

420   heavy to have a purely magmatic signature. However, a small amount of evaporitic material

421   (known to be in the country rocks; Wilson, 1979) may be responsible for the anomalously

422   positive $\delta^{34}S$ value (e.g. Ripley et al. 2003).

423   The dominance of S isotope values less than -2.5 ‰ in sulfides in the intrusion

424   (Supplementary Table S3) indicate that widespread contamination by up to 8 % crustal sulfur

425   (Fig. 12) occurred in the ascending magma at varying depths in the underlying magma

426   plumbing system. Despite this reasonably consistent contamination signature, highly variable

427   sulfide S/Se ratios between olivine gabbros and the rest of the sill suggest that the history of

428   magma contamination in the Magilligan Sill is more complicated than S isotopes imply (Fig.

429   9b). With the exception of the olivine gabbros, all sill units have S/Se between 3 510 and 25

430   200, strongly skewed to higher values that are far removed from the mantle norm of 2 850-4

431   350 (Eckstrand and Hulbert 1987, Queffurus and Barnes 2015). Only the olivine gabbros (S/Se

432   ranging from 1 980 to 3 720) appear to have retained a 'mantle-like' sulfide S/Se signature,

433   despite crustal isotopic input. Modelling the Pd, Se and S/Se concentrations of olivine gabbro

434   and gabbro sulfides yields that they are likely to have had R-factors of around 500-1 000 and

435   10-100, respectively. Modelling results are shown in Supplementary Material S5 and use

436   methods described by Lesher and Burnham (1999).

437   If the sill lithologies represent separate magma pulses (e.g. Fig. 11), the S/Se

438   discrepancy may be the result of largely different degrees of contamination (which contradicts

439     $\delta^{34}S$ signatures in Fig. 9) or, more likely, different S-saturation processes in each pulse

440 (indicated by different R-factors). Olivine gabbro sulfides have evidently lost S (e.g. low S/Se)

441 which could be due to 'cumulative R-factor', a process described by Kerr and Leitch (2005).

442 Sulfide liquids formed during contamination-driven S-saturation in the ascending magma may

443 be cycled upwards in the plumbing system by subsequent magma pulses, towards their final

444 resting horizon (e.g. Hayes et al. 2015). This will subject them to multistage dissolution

445 upgrading, wherein the sulfides are partially dissolved during transportation, reducing their

446 volume and S content while retaining their chalcophile element concentrations (e.g. PGE and

447 Se) (e.g. Kerr and Leitch 2005, Naldrett 2010). We propose that olivine gabbro sulfides in the

448 Magilligan Sill formed in this manner.

449 It should be noted that S loss and low S/Se in sulfides could also be induced by post-

450 magmatic partial oxidation of sulfide minerals, unrelated to S-saturation events (Peck and

451 Keays 1990, Dunn 1997, Queffurus and Barnes 2015). While minor oxidation of sulfides is

452 observed in the olivine gabbros (10-20 %), oxidation is unlikely to explain the significantly

453 lower S/Se ratio of these sulfides in comparison to those in the rest of the sill. For example, if

454 a sulfide grain from a gabbro (initial S/Se = 10 600) undergoes 20% S loss, this would decrease

455 the S/Se to 7 610. In the olivine gabbros, the mean S/Se ratio is 2 940 and if this were to be

456 produced by oxidation of gabbro sulfides alone, it would require a S loss of 72%. Such

457 oxidation should leave clear and visible signs in the olivine gabbro sulfides (e.g. oxide

458 minerals), for which there is no evidence. We conclude that cumulative R-factor is the most

459 likely cause of 'mantle-like' S/Se ratios in the Magilligan Sill.

460 In contrast to sulfides in the olivine gabbros, the lack of detectable trace metals and

461 high S/Se in sulfides from the dolerites and gabbros of the sill (Fig. 10) may imply that this

462 generation of magma remained S-undersaturated throughout ascent, only forming sulfides very

463 locally when contaminated by crustal S from the Waterloo Mudstones at the level of final

464 emplacement. This would inhibit chalcophile sequestration and cumulative R-factor upgrading

21

465   via magma transportation (as envisaged for the olivine gabbro sulfides) (Robertson et al. 2015).

466   This shallow, local S-saturation model is similar to that predicted for basalt dykes on the Isle

467   of Skye (Hughes et al. 2015a). In this way, sulfide (pyrite) formation is akin to very late-stage

468   magmatic-hydrothermal sulfide formation – there was no circulation of sulfide liquid in the

469   magmatic intrusion or feeder and hence no opportunity to equilibrate with the host silicate

470   magma and its chalcophile element content, resulting in base/precious metal poor pyrite. If the

471   base/precious metal bearing second generation sulfides were cycled from upstream in the

472   plumbing system, they may be found in higher (potentially economic) abundances below or

473   adjacent to the Magilligan Sill horizon (e.g. 'earlier' in the system). The change in $\delta^{34}S$ in

474   Figure 10 could potentially represent a diffusion profile, in which the outer parts of the sill (e.g.

475   the dolerites) volatilise and assimilate the most crustal S, reflected in high S/Se and negative

476    $\delta^{34}S$ values that gradually shift to more S-poor values towards interior gabbros. Olivine gabbros

477   disrupt the profile trend, further supporting the hypothesis that they are of a separate injection

478   of magma and different saturation events. Although diffusion via contact metamorphism is a

479   slow process compared to direct crustal assimilation (Robertson et al. 2015), field evidence of

480   the Trotternish Sills report 50-200 cm baked margins of hardened country sediment with

481   minimal surviving sulfide minerals adjacent to the intrusions (e.g. Gibson and Jones 1991,

482   Hughes et al. 2015a). This feature strongly indicates S diffusion was important in triggering S-

483   saturation in Trotternish magmas. Given that there are hornfelsed margins immediately next to

484   the Magilligan Sill, we suggest similar processes could have contributed here too within a

485   comparable timescale.

486   ***Magmatic model***

487   By combining the silicate and sulfide petrography and sulfide compositions, we

488   envisage a final two-stage development model for the Magilligan Sill (Fig. 13). In Stage A, S-

489   undersaturated magma from a deep magma reservoir was emplaced as a sill into the Waterloo

490   Mudstones. Significant contamination of the magma by crustal S only occurred at the current

491   level of emplacement, through contact with the Waterloo Mudstones. This contamination

492   occurred via volatilisation of S from the country rock due to contact metamorphism, or via S

493   addition by direct crustal assimilation. This process was so late-stage and localised that the

494   sulfides within the sill formed under magmatic-hydrothermal conditions. This means that no

495   significant transportation of the sulfide liquid took place within the magma, and little

496   chalcophile elements (for which we use Se as a proxy) entered the sulfide (leading to high S/Se

497   ratios from 3 510 to 25 200 and $\delta^{34}S$ of -9.6 to -2.5 ‰ in the dolerites and gabbros). As a result,

498   sulfides (pyrite and pyrrhotite) crystallising from the S-saturated magma did not sequester

499   chalcophile elements successfully (Naldrett 2010).

500   In the time between the Stage A and B, the dolerites and gabbros were hydrothermally

501   altered (perhaps synchronously with local S volatilisation and pyrite formation) to produce

502   abundant chlorite and clays, and altering olivine phenocrysts to serpentine. In Stage B (Fig.

503   13), the source composition of the magma supply in the conduit system shifted to a more

504   primitive composition so that subsequent magma replenishment in the Magilligan Sill formed

505   the olivine gabbros. S-saturation likely occurred earlier (perhaps deeper) in the magma

506   plumbing system, as indicated by the upgrading processes envisaged for sulfides in the olivine

507   gabbros. Evaporites and mudstones in the Triassic Mercia Mudstone Group or the Permian

508   Belfast Group hundreds of metres below the Magilligan Sill could perhaps have supplied

509   crustal S to Stage B magma, driving it to S-saturation deeper in the system (GSNI 2004).

510   Sulfides (including pyrite, pyrrhotite, chalcopyrite and pentlandite) that segregated from the

511   silicate melt in Stage B contain higher abundances of Ag (< 88 ppm), Co (< 1 460 ppm), and

512   PGE (< 4 ppm). We propose that these sulfides were originally mineralised 'upstream' in the

513   plumbing system that fed the Magilligan Sill. They were cycled through subsequent pulses of

514   second-generation magma before being entrained and emplaced into the Magilligan Sill. The

515   pre-existing dolerites and gabbros formed during Stage A most likely shielded this second pulse

516   of magma (Stage B) from further S absorption from the local country rocks, preventing dilution

517   or addition of late-stage magmatic-hydrothermal S.

518   In this way, the Magilligan Sill, unlike the Trotternish Sills, retains evidence for

519   multiple S-saturation events and pathways between various episodes of magmatic

520   replenishment, as represented by discrete silicate magma pulses. The Southern Feeder Dike

521   Complex of Victoria Island in Canada (part of the Franklin Large Igneous Province) has been

522   interpreted in a similar way, also featuring evidence of conduit-focused magma replenishment

523   and sulfide cycling at different depths in its plumbing system (Hayes et al. 2015). Given that

524   the second-generation sulfides contain PGE, Ni, Cu, Co, and Ag, a higher volume

525   concentration of *in situ* mineralisation of similar or higher tenor nearer the depth at which S-

526   saturation occurred could provide an interesting target for further exploration, despite the

527   Magilligan Sill itself being sub-economic. Since the relatively thin (compared to the southwest)

528   Carboniferous limestones in County Londonderry overlie Proterozoic Grampian basement and

529   both of these contain few S-rich lithologies (GSNI 2004), Permian and Triassic sediments

530   above these appear to be the most logical exploration target for Stage B sulfide-bearing

531   intrusions. Halite beds in the White Brae Mudstone Formation (Permian), sabkha mudstones

532   and halite beds in the Craiganee Formation (Middle Triassic) or dark mudstones in the

533   Westbury Formation (Upper Triassic) are all suitable crustal S contaminants (Wilson 1972). A

534   deeper level of the Magilligan plumbing system in contact with one of these units could

535   potentially be the S-saturation horizon for the olivine gabbro sulfides, and should be the key

536   exploration target for any further Ni-Cu-PGE investigations in the area.

537   **Conclusions**

538   The identification of discrete magmatic pulses within the Magilligan Sill indicate that

539   at least two chemically distinct magma generations were emplaced within a single intrusion.

540   These magma batches may have had significantly different S-saturation pathways and

541   correspondingly different mineralisation potentials. The first magmatic generation crystallised

542   to form most of the sill – olivine-deficient, highly altered dolerites and gabbros with barren

543   sulfide minerals. The second generation crystallised to form olivine gabbro horizons within

544   the pre-existing sill, and contained metal-enriched sulfides. In order to form younger, more

545   primitive magmas, the feeder chamber must have mixed with a new magma between the

546   emplacements of the two different units in the sill, in a similar fashion to the Antrim Plateau

547   Lavas, in which mafic Upper Basalts postdate less mafic Lower Basalts.

548   The S-isotope composition (δ^{34}S) of the Magilligan Sill indicates that crustal S

549   contamination is present throughout the entire intrusion. S/Se ratios in second-generation

550   (olivine gabbro) sulfides are similar to that of published average 'magmatic' values of 2 850-4

551   350 (Eckstrand and Hulbert 1987, Queffurus and Barnes 2015), indicating a deeper S-

552   saturation event perhaps with smaller degrees of crustal contamination. For this reason, sulfides

553   found in the olivine gabbro sections of the sill are interpreted to have formed at depth before

554   being cycled upstream by later magma pulses. The possible controls on this deep S-saturation

555   include: the changing initial composition of the magma at source; the amount of sedimentary

556   S available to the magma via assimilation, and the degree of shielding from these sediments

557   enforced by pre-existing layers of the sill; and the geometry of the magmatic plumbing system.

558   Through a combined approach of S-isotopes, S/Se ratios and detailed petrography, the

559   pathways to S-saturation may be determined within plumbing systems and valuable

560   information fed back into the exploration industry with regards to vectoring towards

561   orthomagmatic sulfide mineralisation, both in the BPIP and more generally for large igneous

562   provinces.

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577

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Table 1 – Average LA-ICP-MS trace element concentrations of sulphides within upper and lower dolerites, gabbros, olivine gabbros and country sediment. * - calculated stoichometrically. † - average concentration of detected isotopes. S = 53.45 wt. % ≈ pyrite; S = 34.94 wt. % ≈ chalcopyrite.

Lithology	S* Wt. %	S/Se	Fe Wt. %	Ni Wt. %	Cu Wt. %	Co ppm	Zn ppm	As ppm	Se ppm	Ru† ppm	Rh† ppm	Pd† ppm
U. Dolerite	53.45	14 279.29	48.60	0.19	0.04	535.455	510.54	19.40	43.32	-	-	-
Gabbro	53.45	10 635.11	44.37	-	0.05	100.70	241.80	20.67	56.21	-	-	-
O. Gabbro	34.94	2 943.03	48.72	6.86	9.26	1 454.59	3 922.32	-	122.89	0.1	0.33	0.64
L. Dolerite	53.45	11 595.33	52.54	0.33	0.10	727.30	3 492.78	355.99	44.79	-	-	-
Sediment	53.45	8117.503	45.02	0.10	0.07	594.90	117.55	1962.31	74.23	-	-	-

Sample	Ag ppm	Cd ppm	Sb ppm	Te ppm	Re ppm	Os ppm	Ir ppm	Pt ppm	Au ppm	Bi ppm	ΣPGE ppm
U. Dolerite	0.94	-	1.74	-	0.2	-	-	-	0.01	0.05	-
Gabbro	2.93	-	3.48	0.86	0.12	-	-	-	-	0.15	-
O. Gabbro	68.54	29.65	0.35	6.00	0.32	0.04	0.04	0.36	0.05	0.88	1.51
L. Dolerite	0.50	-	8.2	0.45	0.02	-	-	-	0.04	0.04	-
Sediment	6.38	0.86	85.59	6.38	0.06	-	-	0.05	0.91	0.65	0.05

Table 2 – Summary S-isotopic compositions of sill and country rock lithologies.

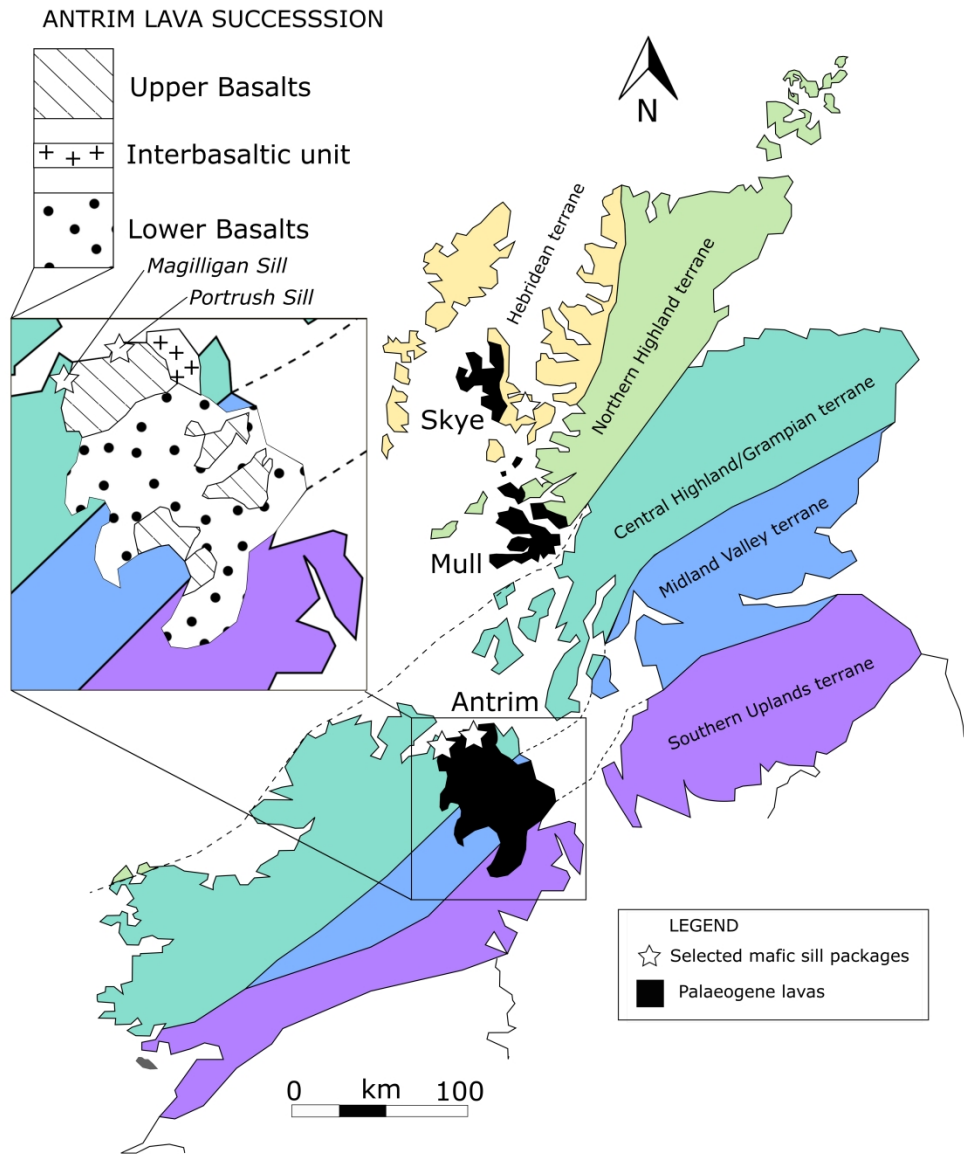| Lithology	Min δ^{34}S ‰	Max δ^{34}S ‰	Mean δ^{34}S ‰	n
Shale (above sill)	-10.00	+5.30	-5.95	4
Upper dolerite	-9.60	-2.50	-6.58	5
Gabbro	+3.40	+3.40	+3.40	2
Olivine Gabbro	-2.50	-1.10	-1.80	2
Lower Dolerite	-2.50	-2.50	-2.50	1
Shale (below sill)	-20.40	-14.90	-17.63	8
Magilligan Sill (overall)	*-9.60*	*+3.40*	*+3.10*	*22*

Figure Captions

Figure 1 – Schematic map of the geology of the BPIP, showing basement units, onshore lavas and notable intrusive complexes. Inset map gives the subdivisions of the Antrim Plateau lavas and the location of the Magilligan and Portrush Sills. Based on work by Woodcock and Strachan (2012).
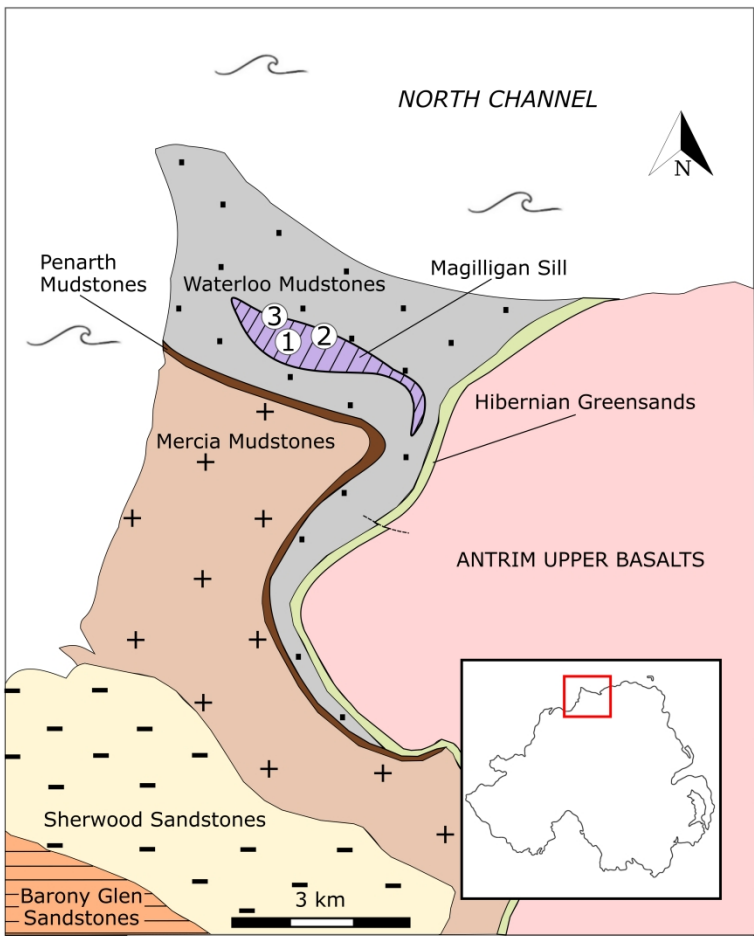
Figure 2 – Schematic geological map of the Magilligan Peninsula, Northern Ireland, indicating the location of the Magilligan Sill and Boreholes 1-3.

Figure 3 – Simplified lithological logs of the Magilligan, Portrush and Trotternish Sills, with their relative intrusion level within the Jurassic stratigraphic columns for Scotland and Ireland. Sill packages are stylised to show multiple injection events. Formation names from Woodcock and Strachan (2012) and GSNI (2004). Portrush and Trotternish relationships from Ledevin (2012), and Gibson and Jones (1991), respectively.

Figure 4 – Representative composite geological log of the Magilligan Sill boreholes. "T" labels show the analysed thin section sample numbers and locations.

Figure 5 – Photomicrographs of Magilligan Sill thin sections: a) Olivine-deficient gabbro (T3) [transmitted light XPL]; b) Olivine gabbro (T7) [transmitted light XPL]; c) Small pyrite grains within gabbro (T2) [reflected light]; d) Large sulphide amalgamation within olivine gabbro, [back-scattered electron image, BSE] (T2). [Pl – plagioclase, Cpx – clinopyroxene, Ol – olivine, Py – pyrite, Po – pyrrhotite, Ccp – chalcopyrite, Pn – pentlandite, Gn – galena]

Figure 6 - Bivariate geochemical plots of a) MgO vs. CaO and b) MgO vs. FeO in analysed clinopyroxenes.

Figure 7 – Bivariate geochemical plots of sulphides in the Magilligan Sill: a) Ni vs. Co; b) Ni vs. Ag; c) Cu vs. total PGE; d) Fe vs. total PGE with respect to mineral phases. Gabbro samples do not contain detectable Ni or PGE.

Figure 8 – Bivariate geochemical plots of sulphides in the Magilligan Sill: a) Se vs. Ni/(Fe+Ni+Cu); b) Se vs. total PGE; c) S/Se vs. total PGE with respect to mineral phases.

Figure 9 – a) Historgram of $\delta^{34}S$ compositions of sulphides in the Magilligan Sill. b) Combined $\delta^{34}S$ vs. S/Se plot for sulphides in the Magilligan Sill, with published magmatic values from Seal (2006) and Quefferus and Barnes (2015). Crosshatched area represents typical magmatic/mantle values.

Figure 10 – Representative downhole variations in lithology (not to scale) combined with S/Se, $\delta^{34}S$, total PGE, Ni, Ag and Cu data from sulphides in these lithologies. Arrows on S/Se and $\delta^{34}S$ plots describe the suggested diffusion profile grading inwards from dolerite to gabbro.

Figure 11 – Petrological development of the Magilligan Sill, showing the two lithological phases found in the intrusion. [Pl – plagioclase, Cpx – clinopyroxene, Ol – olivine, Srp – serpentine, Chl – chlorite, Spl – spinel, Py – pyrite, Po – pyrrhotite, Ccp – chalcopyrite, Pn – pentlandite]

Figure 12 – Binary mixing model for the Magilligan Sill and sedimentary sulphur.

Figure 13 – Stage A in the magmatic development model for the Magilligan system, showing the formation of the dolerites and gabbros, and their barren sulphides. Stage B in the magmatic development model for the Magilligan system, showing the formation of the olivine gabbros, and their cycled base/precious metal sulphides. Model constructed with reference to similar systems in Barnes *et al.* (2016).

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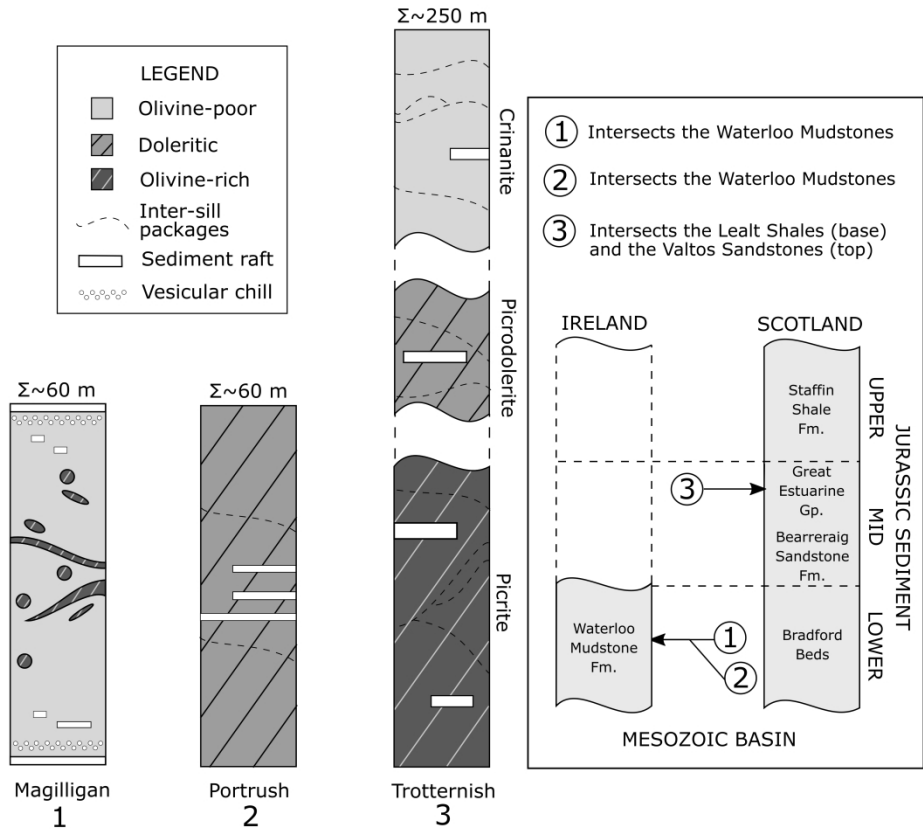
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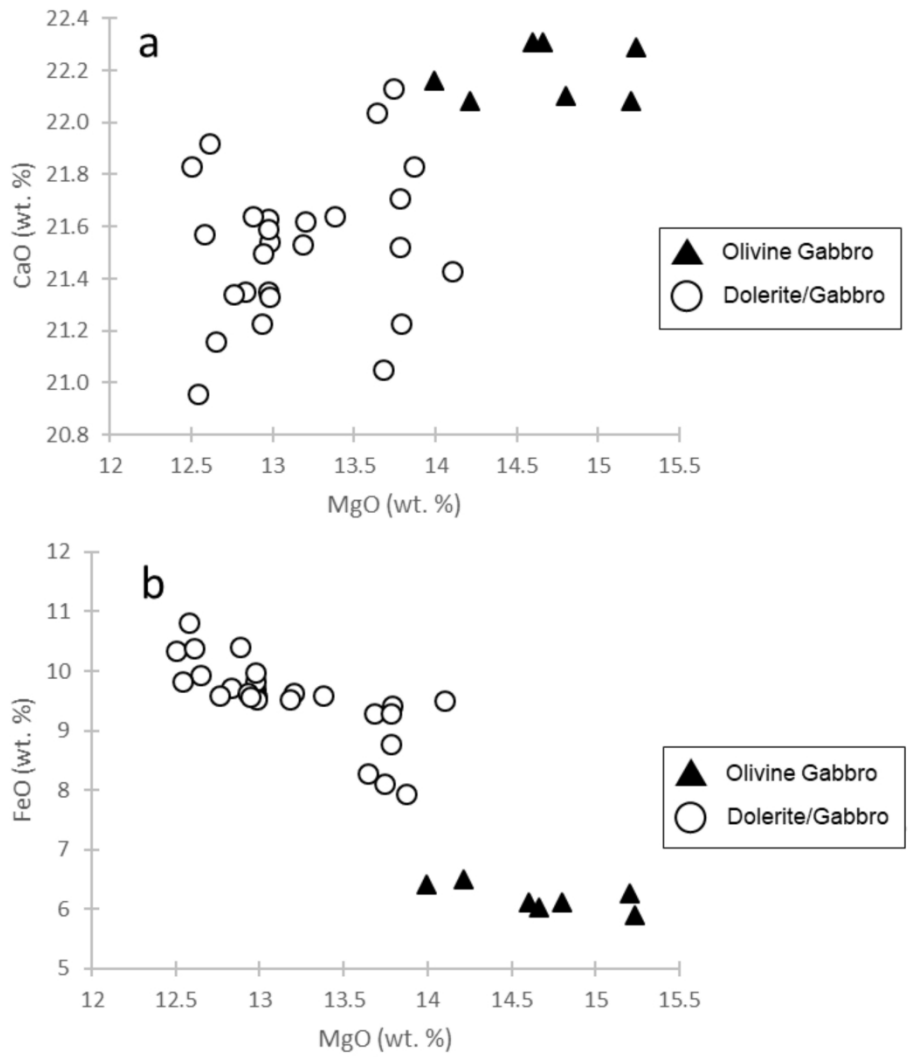
Figure 6 - Bivariate geochemical plots of a) MgO vs. CaO and b) MgO vs. FeO in analysed clinopyroxenes.

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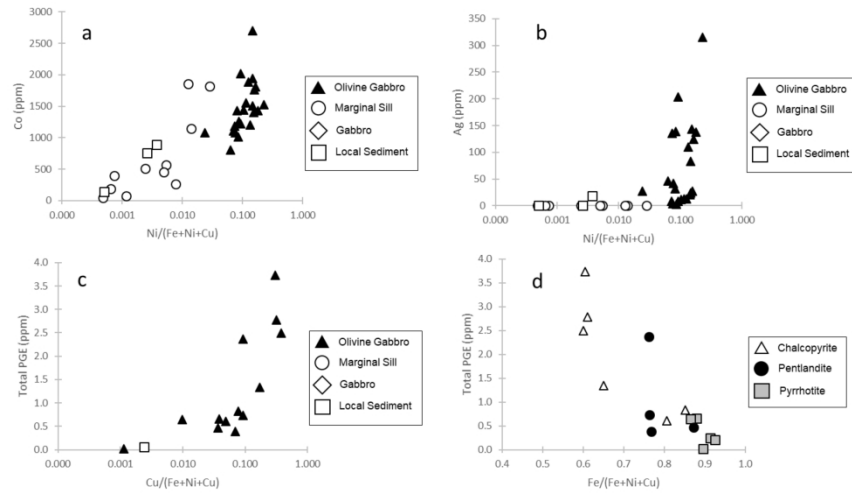
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881x513mm (144 x 144 DPI)

Figure 8 – Bivariate geochemical plots of sulphides in the Magilligan Sill: a) Se vs. Ni/(Fe+Ni+Cu); b) Se vs. total PGE; c) S/Se vs. total PGE with respect to mineral phases.

399x649mm (144 x 144 DPI)

Figure 9 – a) Historgram of δ34S compositions of sulphides in the Magilligan Sill. b) Combined δ34S vs. S/Se plot for sulphides in the Magilligan Sill, with published magmatic values from Seal (2006) and Quefferus and Barnes (2015). Crosshatched area represents typical magmatic/mantle values.
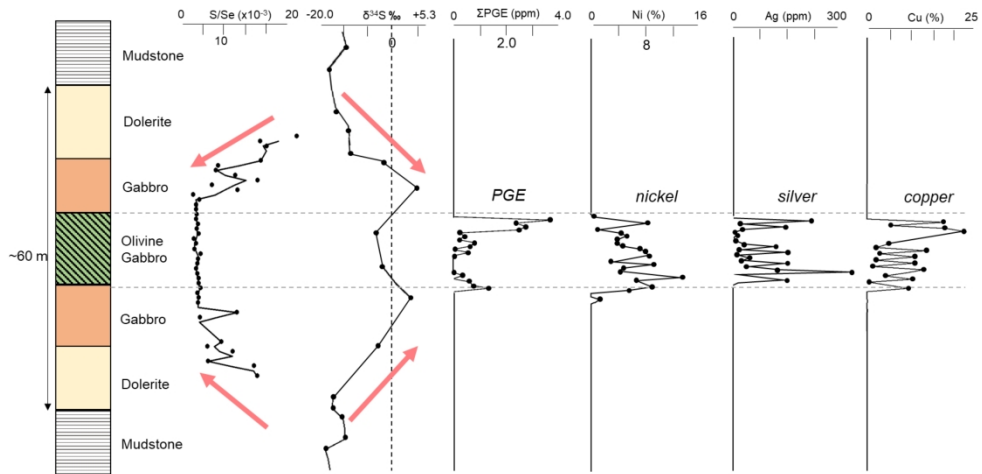
Figure 10 – Representative downhole variations in lithology (not to scale) combined with S/Se, δ34S, total PGE, Ni, Ag and Cu data from sulphides in these lithologies. Arrows on S/Se and δ34S plots describe the suggested diffusion profile grading inwards from dolerite to gabbro.
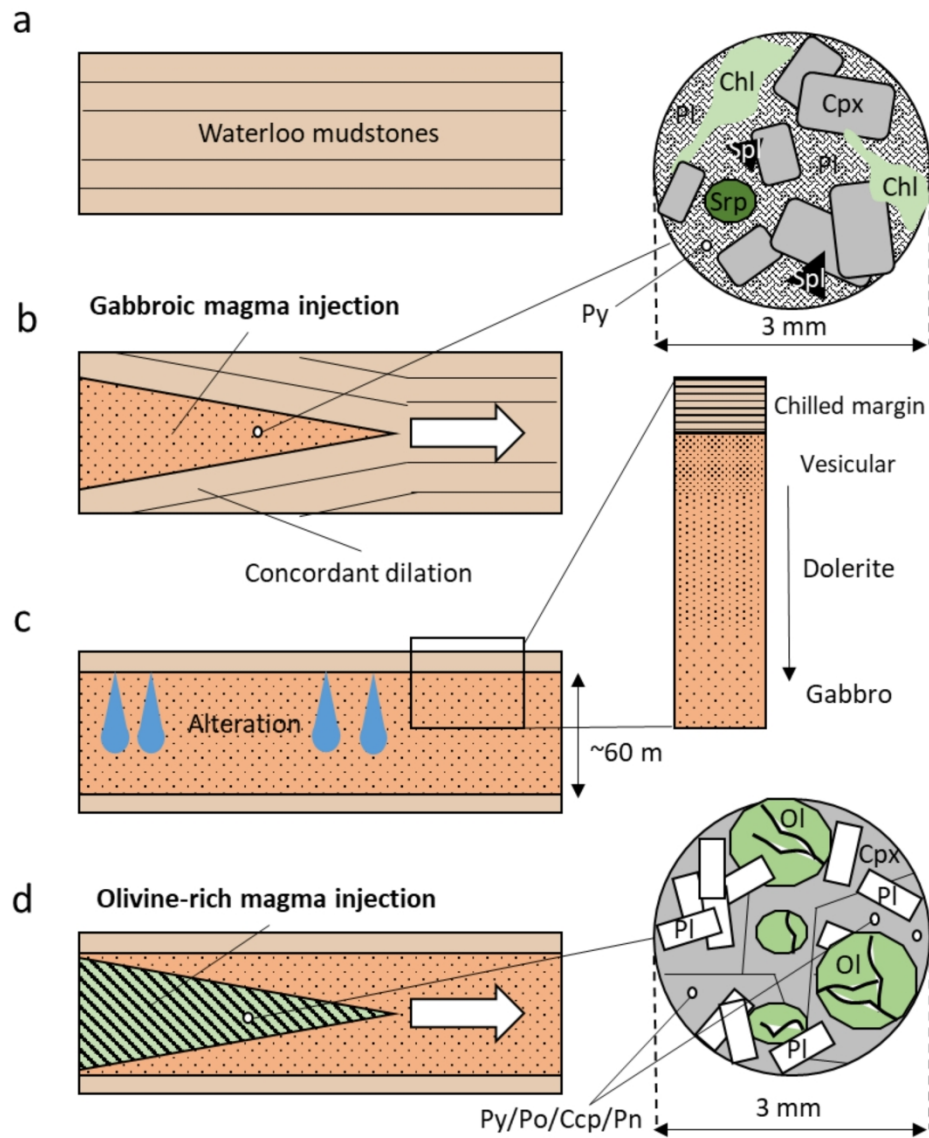
Figure 11 – Petrological development of the Magilligan Sill, showing the two lithological phases found in the intrusion. [Pl – plagioclase, Cpx – clinopyroxene, Ol – olivine, Srp – serpentine, Chl – chlorite, Spl – spinel, Py – pyrite, Po – pyrrhotite, Ccp – chalcopyrite, Pn – pentlandite]
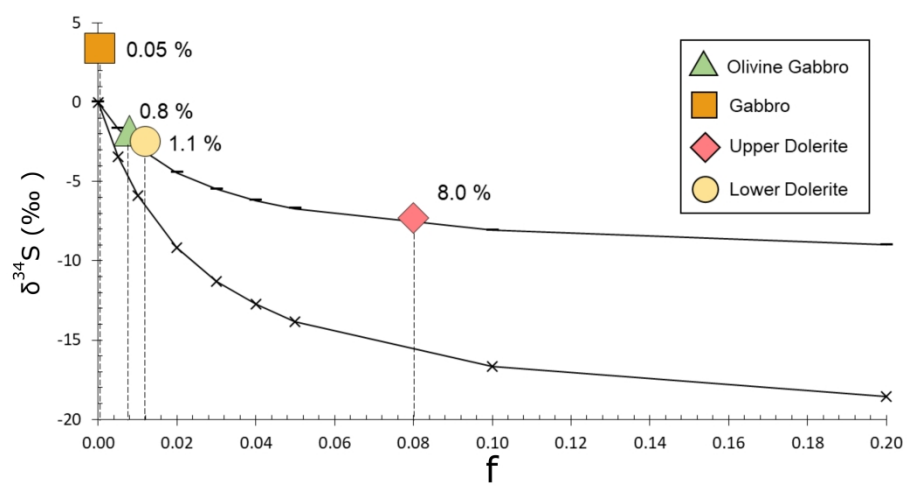
729x895mm (144 x 144 DPI)

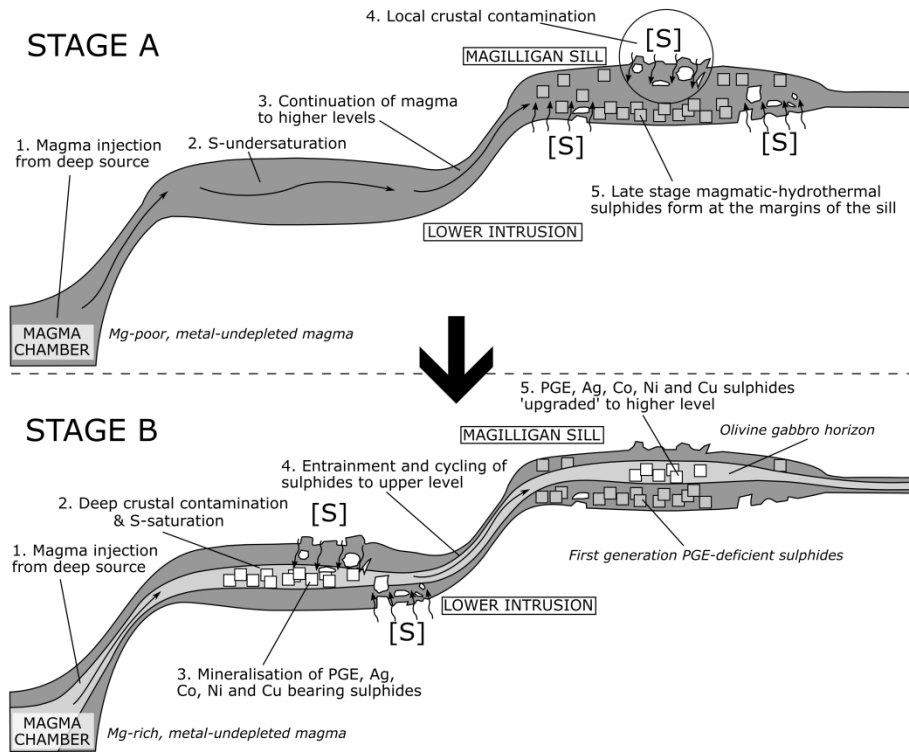Figure 12 – Binary mixing model for the Magilligan Sill and sedimentary sulphur.

Figure 13 – Stage A in the magmatic development model for the Magilligan system, showing the formation of the dolerites and gabbros, and their barren sulphides. Stage B in the magmatic development model for the Magilligan system, showing the formation of the olivine gabbros, and their cycled base/precious metal sulphides. Model constructed with reference to similar systems in Barnes et al. (2016).