Silurian to Devonian magmatism, molybdenite mineralization, regional
 exhumation and brittle strike-slip deformation along the Loch Shin Line, NW
 Scotland.

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16 ABSTRACT

17 The Loch Shin Line (LSL) is a geological-geophysical lineament associated with an 18 anomalous zone of mantle-derived appinites, granites and strike-slip faulting that runs NW-SE across the Moine Nappe from the Moine Thrust to the Moray Firth. U-19 20 Pb zircon and Re-Os molybdenite dating of the Loch Shin and Grudie plutons that lie 21 to immediately south of the NW-SE Loch Shin-Strath Fleet fault system yields ca 22 427-430Ma ages that overlap within error. They also coincide with previously 23 obtained U-Pb zircon ages for the Rogart pluton which lies along strike to the 24 southeast. Field and microstructural observations confirm the similarity and 25 contemporaneous nature of the plutons and associated sulphide mineralisation. 26 Fluid inclusion analyses place further constraints on the P-T-X conditions during 27 regional late Caledonian exhumation of the Moine Nappe in this part of NW Scotland. 28 Synchronous to slightly younger (ca 410Ma?) brittle dextral strike slip faulting along 29 the WNW-ESE Loch Shin-Strath Fleet Fault System was likely antithetic to regional 30 sinistral strike-slip movements along the NE-SW trending Great Glen Fault. Our 31 findings lend support to the hypothesis that the LSL acted as a deep crustal

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channelway controlling the ascent and emplacement of Silurian granitic and
appinitic magmas into the overlying Moine Nappe. We propose that this deep
structure corresponds to the southeastern continuation of the Precambrian-age
Laxford Front shear zone in the buried Lewisian autochthon.

36

37 **INTRODUCTION**

38 It is well established that orogenic belts worldwide are characterized by interlinked 39 systems of thrust, strike slip and extensional faults and, at deeper crustal levels, by 40 shear zones that collectively accommodate crustal deformation during plate 41 collision (e.g. Dewey *et al.* 1986). In general, this leads to the development of broad, 42 diffuse regions of 'block and flake tectonics' where plate motions are partitioned 43 into complex displacements, internal strains and rotations. The location, geometry 44 and persistence of faults and shear zones in such regions are known to be influenced 45 directly by the presence and reactivation of crustal-scale pre-existing structures 46 (Sutton & Watson 1986; Holdsworth et al. 1997, 2001). These same structures are 47 also known to act as channelways that control the upward migration and 48 emplacement of hydrous mineralizing fluids and magmas (e.g. O'Driscoll 1986; 49 Hutton 1988a; Jacques & Reavy 1994; Richards 2013). This coincidence of 50 geological processes has greatly assisted in the analysis of orogenic deformation 51 histories worldwide since dating of igneous intrusions and/or mineralization events 52 using geochronology can also be used to constrain the absolute ages of associated 53 deformation events in the adjacent wall rocks (e.g. Paterson & Tobisch 1988; 54 Schofield & D'Lemos 1998; Rosenberg 2004).

55 Integrated structural and geochronological studies of deformed igneous intrusions have played a key role in constraining the timing of events within the 56 57 Early Palaeozoic Caledonian orogeny in Scotland (Fig. 1a). Following Ordovician arc 58 continent collision (the Grampian event), the final closure of lapetus involved the 59 oblique collisions of three palaeo-continents: Laurentia, Baltic and Avalonia during 60 the mid- to late Silurian (e.g. Soper et al. 1992; Torsvik et al. 1996). In NW Scotland, 61 regional deformation occurred due to the sinistral oblique Scandian collision of 62 Baltica with Laurentia. Crustal thickening here was overlapped and followed by 63 major sinistral displacements along orogen-parallel strike-slip faults such as the 64 Great Glen Fault (GGF; Fig 1a) heralding a transition from a regime of sinistral 65 transpression to transtension (Dewey & Strachan 2003 and references therein). 66 Igneous activity and associated mineralization related to slab breakoff was 67 associated with every stage of this transition, with earlier granites syn-tectonically 68 emplaced along Scandian thrusts (e.g. Naver Thrust, see Holdsworth & Strachan 69 1988; Kinny et al 2003; Goodenough et al. 2011; Kocks et al. 2013), whilst later, 70 volumetrically larger volumes of melt were emplaced along steeply-dipping strike-71 slip or normal faults (e.g. Great Glen Fault; Hutton 1988b; Hutton & McErlean 1991; 72 Jacques & Reavy, 1994; Stewart *et al.* 2001). In many cases the controlling faults or 73 shear zones are exposed at the present-day surface, but others are more enigmatic features. As illustrated by Jacques & Reavy (1994) they are commonly inferred 74 75 'buried' structures based on geological, geophysical or geochemical alignments that 76 define regional scale transverse lineaments that run generally at high angles to the 77 orogenic strike. One of these NW-SE features, the Loch Shin Line (LSL) - first

78 defined by Watson (1984) – is associated with an anomalous zone of mantle-derived 79 appinites, granites and brittle faulting in the Moine Nappe SE of the Moine Thrust on 80 the N side of the Assynt culmination (Fig. 1a, b). The LSL follows a strong NW-SE 81 gravity gradient that defines the NE margin of a strong negative anomaly centred on 82 the Grudie Granite (Figs 1b, see Leslie et al. 2010 and references therein). Watson 83 (1984) suggested that the LSL corresponds to the presence of a Precambrian shear 84 zone in the Lewisian autochthon underlying the Moine Nappe and that this shear 85 zone has controlled the siting and ascent of magmas and associated mineralization 86 during the Silurian. The dextral faulting that follows the trend of the LSL defines the 87 Loch Shin, Strath Fleet and Dornoch Firth fault systems (Fig. 2a; Strachan & 88 Holdsworth 1988) which are thought to be part of a regional fault set antithetic to 89 the regional sinistral movements along faults such as the GGFZ (see Johnson & Frost 90 1977; Watson 1984). The Rogart igneous complex (Fig. 1a; Soper 1963), a large 91 composite igneous intrusion of mantle derivation that lies on the NE margin of the 92 LSL, is bounded to the SW by the Strath Fleet Fault. Kocks et al. (2013) have shown 93 that emplacement of the central pluton – dated at 425±1.5 Ma using U-Pb (TIMS) 94 zircon - was likely controlled by dextral motions along the LSL. These authors used 95 this evidence to date the switch from sinistral transpression with thrusting to 96 transtension with regional strike slip faulting at ca. 425 Ma.

97 The present paper re-examines this hypothesis in the region of Loch Shin 98 where two plutons notably associated with a zone of molybdenite mineralization 99 hosted in Moine and Lewisian country rocks (Gallagher & Smith 1976) are poorly 100 exposed: the Loch Shin and Grudie granites (Figs 1 & 2). Field observations and

101 microstructural studies are used to constrain the geometry, kinematics and relative 102 ages of deformation in the plutons and country rocks, whilst U-Pb zircon and Re-Os 103 molybdenite geochrology are used to date both pluton emplacement and the 104 spatially associated mineralization. Finally, fluid inclusion studies are used to 105 further constrain the P-T-X conditions during deformation and igneous 106 emplacement and assess the relationships between regional structures such as the 107 LSL and fluid flow.

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109 **GEOLOGICAL SETTING**

110 The Loch Shin area is mostly underlain by variably deformed metsedimentary rocks 111 of the Morar Group, part of the Neoproterozoic Moine Supergroup in NW Scotland 112 (Figs 1, 2; Holdsworth et al. 1994; Strachan et al. 2010). To the northwest, the Moine 113 Nappe is bounded by the underlying Moine Thrust and Moine Thrust Zone, whilst to 114 the north and east it is overlain by the Naver Thrust which carries the Loch Coire Migmatite Complex (Fig. 1a; Kocks et al. 2013). Zircon U-Pb geochronology shows 115 116 that the migmatite complex formed during the Ordovician Grampian event ca 470-117 460Ma (Kinny et al. 1999). This was then followed by generally top-to-the-NW 118 Scandian ductile thrusting with early displacement along the Naver Thrust, followed 119 by later thrusts propagating progressively towards the Caledonian foreland ending 120 with the development of the Moine Thrust Zone (Barr et al. 1986; Johnson & 121 Strachan 2006; Alsop *et al.* 2010; Leslie *et al.* 2010). Zircon U-Pb dating of various 122 syn-kinematic igneous intrusions constrains thrust movements to have occurred ca. 123 435-425Ma (Kinny et al .2003; Kocks et al. 2006; Goodenough et al. 2011). The

broad regional arcuate swing of the regional foliation and ductile thrusts within the
Moine and Naver nappes (Fig. 1a, 2a) is attributed to the development of the Cassley
structural culmination and regional-scale flexuring in the rocks overlying the Assynt
thrust culmination (Elliott & Johnson 1980; Butler & Coward 1984; Leslie *et al.*2010).

129 The Loch Shin and Grudie granites are hosted in Moine Supergroup rocks 130 belonging to the Morar Group which are locally interleaved with antiformal isoclinal 131 infolds of their underlying Lewisianoid basement (Read et al. 1926; Gallagher & 132 Smith 1976; Strachan & Holdsworth 1988; Leslie et al. 2010). The Moine rocks are 133 mostly unmignmatized psammites interlayered with subordinate semipelitic and 134 pelitic horizons preserving rare sedimentary structures such as cross-lamination 135 and grading in areas of low tectonic strain. The Lewisianoid rocks are typically 136 lithologically diverse and include hornblendic and quartzofeldspathic gneisses, 137 amphibolites and subordinate units of ultramafic hornblendite, together with thin 138 strips of metasedimentary schist and marble (e.g. as seen on the Airde of Shin, Fig. 139 2a; Strachan & Holdsworth 1988 and references therein). Individual Moine-140 Lewisianoid boundaries - where exposed - are marked either by the development of 141 local basement conglomerates or by the development of mica-rich 'tectonic schists' 142 (e.g. Airde of Shin; Fig 2a) (Peacock 1975; Strachan & Holdsworth 1988).

143 The dominant structures in the Moine and Lewisianoid rocks are tight to 144 isoclinal D2 folds that carry an axial planar S2 crenulation fabric of an earlier 145 bedding parallel schistosity (S1). The main foliation is therefore in general a 146 composite S0/S1/S2 fabric which carries an ESE- to SE-plunging mineral extension

lineation L2 (Strachan & Holdsworth 1988). This lineation is interpreted to lie
parallel to the regional direction of top-to-the-NW tectonic transport during
Scandian thrusting (e.g. Barr *et al.* 1986; Strachan *et al.* 2010). Associated regional
metamorphism during D2 in the Loch Shin area was within the low to midamphibolite facies (Soper & Brown 1971; Strachan & Holdsworth 1988).

152 The Moine and Lewisianoid rocks around Lairg and Loch Shin are cut by a 153 number of granitic bodies, which include (from largest to smallest): the Grudie, 154 Claonel and Loch Shin intrusions (Fig. 2; Gallagher & Smith 1976), together with 155 numerous small associated sheets and plugs of similar composition. These fall into 156 two distinct groups: early foliated granodiorites (Claonel), thought to be directly 157 equivalent to parts of the Rogart igneous complex, and supposedly later, generally 158 unfoliated intrusions of pink adamellite including the Grudie and Loch Shin bodies. 159 The trace of the LSL is also marked by a concentration of small plugs and pipe-like 160 bodies of intermediate to ultramafic appinites known locally as the Ach'uaine 161 hybrids (Fig. 1b; Read et al. 1925; Watson 1984). These also occur as comagmatic 162 enclaves within the ca. 425Ma central granodiorite of the Rogart igneous complex 163 (Fowler et al. 2001; Kocks et al. 2013). Appinitic intrusions are widely associated 164 with late Caledonian plutons throughout the Scottish Highlands and point to a 165 significant mantle contribution to this magmatism (e.g. see Fowler & Henney 1996; 166 Fowler *et al.* 2008).

167 Regional mapping, stream sediment sampling and analysis of shallow 168 borehole cores in the Loch Shin-Grudie area has shown that low grade molybdenite 169 mineralization is associated with pyrite in thin post-foliation quartz veins cutting

both country rock and granites; subordinate chalcopyrite, fluorite, galena, barite and
sphalerite also occur (Gallagher & Smith 1976). This mineralization is spatially
associated with the granites, but Gallagher & Smith (op cit) suggest that it may also
have been significantly influenced by regional structures in the surrounding wall
rocks.

175 Between Loch Shin and the Moray Firth to the east, the Moine and Lewisian 176 rocks are cut by at least three major, sub-vertical brittle faults: the Loch Shin, Strath 177 Fleet and Dornoch Firth fault zones (Fig. 1a; Read et al. 1925, 1926; Strachan & 178 Holdsworth 1988; Kocks et al. 2013). Exposure of the fault zones is generally very 179 poor and only the Strath Fleet fault has been previously studied in any detail (Soper 180 1963). A series of NW-SE-trending steeply dipping crush zones were recognized 181 that overprint Moine country rocks, the Rogart igneous complex and unconformably 182 overlying Devonian basal conglomerates (middle Old Red Sandstone). There is 183 evidence for multiple fault movements, with cataclastic fault rocks included as clasts 184 within overlying Devonian conglomerates and minor intrusions that cut brittle fault 185 rocks whilst also being overprinted by later faulting (Soper 1963). However, there is 186 little published evidence to support the dextral shear sense inferred by many 187 authors along these NW-SE faults (e.g. Johnson & Frost 1977; Watson 1984), 188 although apparent regional offsets of regional boundaries in the Moine Nappe are 189 consistent with right-lateral movements along the Strath Fleet and Dornoch Firth 190 Faults (Fig 1a; Soper 1963; Strachan & Holdsworth 1988). A presumably late 191 (?Devonian) NE-side-down movement is also inferred for the Strath Fleet Fault

based on the preservation of Devonian conglomerates in an elongate NW-SEtrending outlier that follows the Strath Fleet Valley (e.g. see Kocks *et al.* 2013).

194 There are no published structural studies of any of the igneous bodies that 195 occur close to Loch Shin due to the extremely poor levels of exposure (<1%). The 196 Grudie pluton is inferred to cross-cut all ductile fabrics and geological boundaries in 197 the Moine and Lewisian rocks based on the obviously discordant nature of the 198 mapped boundaries and the absence of an internal foliation (Fig. 2b; Gallagher & 199 Smith 1976). The present study focusses on two key areas of exposure: a ca 1 km 200 long sporadically continuous section through Moine rocks and part of the Loch Shin 201 Granite on the southwest shore of Loch Shin; and isolated exposures of Grudie 202 Granite exposed in road cuts related to the Meall a Gruididh wind farm development 203 (Fig. 2b).

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205 LOCH SHIN GRANITE

Good quality water-washed exposures of Moine country rocks, the Loch Shin Granite and associated mineral veins occur along the SW shore of Loch Shin between NC 5650 0590 and NC 5625 0668 (Fig. 2b). Isolated poor quality exposures also occur in inland areas and stream sections, notably along the Allt a'Chlaonaidh (see Gallagher & Smith 1976, fig. 3).

Moine country rocks are exposed south of the Loch Shin granite between NC 5650 0590 and NC 0623 5638 and, north of the granite, between NC 5625 0668 and NC 5587 0766. They are for the most part fine to medium grained grey mica psammites with a flaggy foliation and mm-scale compositional banding (Fig. 3a).

215 Isolated layers of grey-brown weathering semipelite-pelite are sparsely developed 216 in layers up to 20cm thick. In thin section, the psammites typically comprise quartz, 217 plagioclase, K feldspar, green biotite and accessory phases (mineralization, garnet, 218 epidote). Quartz and feldspar uniformly display sub-equant polygonal to cuspate-219 lobate textures typical of amphibolite facies conditions (e.g. see Holdsworth & Grant 220 1990), with the main banding parallel fabric (S0/S1/S2) being defined primarily by 221 aligned biotite grains (Fig. 3b). The foliation and associated mineral lineations are 222 locally variable in orientation – possibly due to the local effects of late brittle folding 223 and faulting (see below) - but the majority strike NE-SW with moderate SE dips 224 (Figs 2b, 4a). The associated fine mineral lineations, interpreted here as L2, plunge 225 mainly ESE (Fig. 4a) as is typical of this part of the Moine Nappe in Sutherland (e.g. 226 Strachan & Holdsworth 1988).

The ductile foliation in the Moine rocks is cross cut at low angles by a number of generally NE-SW trending, moderately SE dipping pink granite and granite pegmatite sheets up to 1m thick (e.g. Figs 3a, 5b). These are unfoliated and are compositionally very similar to the main Loch Shin granite.

The contacts of the Loch Shin granite are not exposed but are inferred to trend NE-SW and dip to the SE (Figs 2b, 4b). The pink granite is typically fine to medium grained and is unfoliated, lacking both magmatic and solid-state ductile fabrics (Fig. 3c, d). In thin section it typically comprises weakly sericitised plagioclase, perthitic K-feldspar (occasionally as phenocrysts), quartz, biotite (often altered to secondary chlorite) and iron oxide (?magnetite). The granite appears to be fairly homogneous in terms of both composition and grain size and no internal

contacts were seen. No magmatic-state fabric is present, nor is there any evidence of
crystal plasticity other than low-temperature features spatially associated with
fractures.

241 The granite is cut by irregular sets of quartz-pyrite-chalcopyrite veins (Fig. 242 3e) with rare molybdenite. These appear to occur in a variety of orientations and no 243 particular trend seems to dominate. However, at NC 5630 0660, a large subvertical 244 SSE-NNW trending quartz-pyrite-sphalerite-chalcopyrite-galena vein up to 1 m 245 thick is exposed (Fig. 3f) and can be traced for over 10 metres along strike. The 246 veins also lack ductile deformation fabrics, but are cross cut by brittle faults and the 247 effects of low temperature cataclasis (e.g. Fig. 5a). Rice & Cope (1973) and Gallagher 248 & Smith (1976) give further details of veins and mineralization found in the 249 surrounding Moine and Lewisian rocks and report the additional presence of minor 250 amounts of covellite, barytes and fluorspar. Rare, late veins of zeolite <1mm thick 251 were observed cross-cutting fault-related breccias in Moine host rocks (e.g. NC 5625 252 0668).

253 Brittle deformation is widely recognized cutting both Moine country rocks, 254 the Loch Shin Granite and associated granite-pegmatite veins (Figs 5a-f). The Loch 255 Shin Granite is cut by a series of steeply-dipping, several metre long, very planar 256 dextral faults trending WNW-ESE with shallowly plunging slickenlines (Figs 4c, 5c). 257 The total offsets are unknown. Dextral faults are everywhere associated with 258 shorter length, steeply-dipping N-S to NE-SW sinistral faults with cm-scale offsets 259 (Figs 4c, 5a) which either abut against or are cross-cut by dextral faults (Fig. 5d) suggesting that they are contemporaneous. A subordinate set of irregularly oriented, 260

261 mainly shallowly-dipping reverse faults with prominent NNW- to SSE-plunging 262 grooves & slickenlines is locally present in the granite outcrops (e.g. around NC 263 5635 0630; Figs 4d, 5e). The fault planes are notably curvilplanar & lineated, with a 264 series of ramp-flat configurations. Offsets are mostly small (mm-cm scale). Once 265 again these faults show mutually cross-cutting relationships with the steeply 266 dipping strike slip faults suggesting that they are broadly contemporaneous. A 267 stress inversion analysis of all fault slickenline data suggests a normal faulting to 268 transtensional stress regime with a component of N-S shortening and E-W extension 269 consistent with regional-scale dextral shear along the Loch Shin Fault (Fig 4f).

270 In addition to brittle faults, both Moine rocks and granite are locally cut by 271 metre-scale zones of brecciation and cataclasis, some of which appear to be 272 associated with specific faults whilst others seem to be diffuse and irregular. The 273 banded Moine rocks locally preserve brittle-ductile box folds with generally 274 moderate to steep easterly plunges (e.g. Figs 4e, 5f). These structures refold the 275 ductile foliation (S2) and lineation (L2). The age of these folds relative to granite 276 emplacement is uncertain, but one example appears to detach along a NE-SW 277 sinistral fault suggesting that the folds are also post-granite features related to the 278 regional brittle deformation. Such folds have not been observed within the granite, 279 but it is suggested that this may be due to a lack of pre-existing mechanical layering 280 in the igneous host rocks.

In thin section, the effects of brittle deformation and cataclasis are widespread in all rocks along the Loch Shin shore section (e.g. Figs 6a-f). Irregular networks of small offset shear and hybrid fractures host variable amounts of

284 mineralization and secondary alteration features including sericite and other clay 285 minerals, quartz, chlorite, hematite, pyrite, chalcopyrite, limonite, fluorite and 286 zeolite (e.g. Figs 6c, e, f). This suggests that the fractures have hosted significant 287 volumes of fluid, an assertion supported by the widespread preservation of multiple 288 sets of healed microfractures (Tuttle lamellae) in quartz in a wide range of 289 orientations (Figs 6d, e). The presence of both pyrite and chalcopyrite in these 290 fracture fills suggest that at least some of the widely observed base metal 291 mineralization was synchronous with brittle deformation. In several cases, sericite-292 filled fractures cutting feldspars are seen to pass laterally into well-defined Tuttle 293 lamellae in adjacent quartz grains (Fig. 6e). Isolated veins of zeolite <1mm thick 294 cross cut all other brittle structures (Fig. 6f) and appear to represent the final phase 295 of mineralization.

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297 **GRUDIE GRANITE**

298 The Grudie Granite is exceptionally poorly exposed and none of its contacts have 299 been observed, although the mapped relationships suggest that it is highly 300 discordant with the foliation in the surrounding Moine and Lewisianoid wall rocks 301 (Fig 2b). In surface exposures, the granite is entirely unfoliated, is medium to fine 302 grained, with sparse large phenocrysts of perthitic K-feldspar up to 1cm across and 303 large rounded xenocrysts of polycrystalline quartz up to 1cm across (Fig. 7a-d). 304 These are set in a matrix of lightly to moderately sericitized plagioclase and quartz, 305 with sparse K-feldspar, biotite and iron oxide. Little internal variation in grain size 306 or mineralogy has been observed and internal contacts were not found.

In the field, well-developed joints carry epidote, chlorite, zeolite, iron and manganese oxides with slickenlines locally developed in a variety of orientations, mainly dip-slip or oblique slip (Fig. 7b). In thin section, the effects of brittle deformation are limited with small fractures filled mainly with epidote, white mica, chlorite and limonite. The overall level of fracturing is much less when compared to the Loch Shin Granite (e.g. Figs 7c, d).

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314 ZIRCON U-Pb ISOTOPE ANALYSIS

315 Sample, mineral separation and analytical protocols

316 A representative sample of Loch Shin granite from the SW west shore of Loch Shin 317 (DS1-11; Fig. 2b, NC 5635 0625) was selected for Zircon U-Pb LA-ICP-MS 318 geochronology. Zircons were separated from sample DS1-11 using heavy liquids and 319 an isodynamic magnetic separator. The zircon fraction for analysis was handpicked 320 under a binocular microscope and mounted in epoxy resin along with grains of the 321 zircon reference material Temora 2 (Black *et al.* 2004). After polishing and carbon 322 coating, cathodoluminescence (CL) images of the zircons were taken with a KeDev Centaurus CL detector housed on a JEOL 6060LV SEM at the University of 323 324 Portsmouth (accelerating voltage = 15 kV) (Fig. 9).

Laser ablation (LA)-ICP-MS U-Pb isotope analyses were undertaken at the University of Portsmouth, using a New Wave 213 nm Nd:YAG laser coupled with an Agilent 7500cs quadrupole ICP-MS. Analytical protocols and instrument conditions are described in detail by Darling *et al.* (2012). Key points of the methodology are: (i) line-raster ablation (aspect ratio 1:1.5), in order to minimise time-dependent

330 elemental fractionation; and (ii) external normalisation to the zircon standard 331 Plesovice (Slama *et al.* 2008) using a 30 µm beam diameter. Laser beam diameters 332 used on unknown zircons ranged from 30 to 15 µm, reflecting the scale of target 333 domains within the crystals. Accuracy was monitored via analyses of the zircon 334 reference materials Temora 2 and GJ-1. Eight analyses of Temora 2 (20 to 30 µm 335 beam diameter) yield a U-Pb concordia age of 417.4 ± 3.5 Ma, and eight analyses of 336 GJ-1 (30 µm beam diameter) yield a U-Pb concordia age of 606.6 ± 3.8 Ma: both of 337 which are within uncertainty of the ID-TIMS reference ages for these materials 338 (Black et al. 2004, Jackson et al. 2004).

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340 Results

341 The zircons separated from sample DS1-11 are generally small (<120 μ m in length). 342 The majority of the zircons possess euhedral to sub-euhedral prismatic forms, with 343 oscillatory or banded zonation textures as revealed by CL imaging (Fig. 8). 344 Approximately 15 percent of grains are significantly different, and have variable 345 habit from equant to elongate with sub-euhedral to anhedral forms. The CL textures 346 of these grains are also variable, including sector zonation, broad banding and 347 oscillatory zonation with spongy overgrowths. A total of 19 zircon grains were 348 analysed by LA-ICP-MS, including a range of textural types (Table I). Three analyses 349 were rejected due to high levels of ²⁰⁴Pb (common Pb), which was not corrected for 350 during data reduction.

The majority of the analyzed grains yield Silurian ages, although there is one concordant analysis with a 207 Pb/ 206 Pb age of 1284 ± 19 Ma and three slightly

353 discordant analyses with ²⁰⁷Pb/²⁰⁶Pb ages ranging from 1725 to 1771 Ma (Table I, 354 Fig 9a; all age uncertainties given to two standard deviations). These older grains 355 are of the equant, anhedral group and have Th/U ratios (0.4-0.6) that are 356 significantly lower than the Silurian grains (Th/U = 0.9 to 1.5). Ten of the prismatic, 357 more euhedral grains with oscillatory zonation textures yield ²⁰⁶Pb/²³⁸U ages 358 ranging from 416 to 436 Ma (Fig. 9b). In combination, these grains yield a concordia 359 age of 427.3 ± 3.7 Ma. Two additional analyses yielded discordant U-Pb isotope data, 360 and fall on a discordia line between the younger concordant population and ca. 361 1700 Ma. These are interpreted as mixed analyses, which is supported by the 362 observation of variable isotopic ratios in the time resolved signals. The 427.3 ± 3.7 363 Ma concordia age of the younger group of prismatic zircons, with CL textures 364 (oscillatory or fine-banded) and Th/U ratios (0.9-1.5) typical of igneous zircon, is 365 taken as the best estimate of intrusion age of the Loch Shin Granite (Fig. 10).

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367 RHENIUM-OSMIUM MOLYBDENITE GEOCHRONOLOGY

368 Samples

Four molybdenite samples were collected for rhenium-osmium (Re-Os) geochronology to constrain the timing of sulphide mineralization associated with the Loch Shin and Gruide granite intrusions. Although molybdenite mineralization was noted in several places within the Loch Shin intrusion by Gallagher & Smith (1976) only one *in-situ* quartz-molybdenite vein was observed in the field (AF33-10; NC 5614 0650; Fig. 2b). The ~1cm quartz vein hosts minor fine grained (~1mm) rosettes and disseminated molybdenite grains. No appreciable alteration selvage is

376 present, with the exception of minor silicification, and chlorization of magmatic377 biotite.

378 Three additional samples were selected from the area around the Grudie 379 granite and molybdenite±pyrite mineralization sufficient for geochronological 380 analysis was only observed in the neighboring Moine rocks adjacent to the intrusion 381 (Fig. 2b). The mineralization post-dates all ductile Moine fabrics. Molybdenite 382 mineralization is associated with and without quartz veins and, similar to the Loch 383 Shin granite, wallrock alteration is limited to silicification, and chloritization of 384 biotite in the Moine rocks. Molybdenite within quartz veins is fine grained (0.5 to 385 1mm) and occurs as disseminations and parallel to the boundary between the 386 quartz vein and wallrock (AF01-11; AF02-11). Molybdenite also occurs as coatings 387 along fractures (AF36-10).

388

389 Mineral separation and analytical protocol

Molybdenite samples present in the area of the Grudie Granite were isolated using traditional methods of crushing, heavy liquids, and water floatation (Selby & Creaser, 2004). In contrast, given the minor abundant of molybdenite in the Loch Shin Granite sample (AF33-10), and to avoid losing molybdenite during crushing, the mineral separate was achieved using a room temperature HF dissolution of quartz protocol (Lawley & Selby, 2012).

The Re-Os analysis follows that outlined by Selby & Creaser (2004), which determines the Re and Os abundance of the molybdenite using isotope dilution negative thermal ionization mass spectrometry (ID-NTIMS). An aliquant of

399 molybdenite, together with a known amount tracer solution (isotopically normal Os 400 + ¹⁸⁵Re) are digested and equilibrated in a carius tube with 1mL 11N HCl and 3mL 401 15N HNO₃ for 24hrs at 220°C. Osmium is isolated and purified from the acidic 402 solution using solvent extraction $(CHCl_3)$ and micro-distillation methods. The Re is 403 separated and purified using anion chromatography. The separated Re and Os were 404 loaded on Ni and Pt wire filaments with BaNO₃ and BaOH activators, respectively, 405 and analyzed for their isotope compositions using NTIMS via static Faraday 406 collection. Analytical uncertainties are propagated and incorporate uncertainties 407 related to Re and Os mass spectrometer measurements, blank abundances and 408 isotopic compositions, spike calibrations, and reproducibility of standard Re and Os 409 isotope values. The molybdenite analyses of this study were conducted during the 410 same period as those of Lawley & Selby (2012). This study reported Re and Os 411 blanks of <4 and 1 pg, respectively, with the 187 Os/ 188 Os of the blank being 0.25 ± 412 0.02 (n = 2). Further, Re-Os model ages determined using the 187 Re decay constant 413 of 1.666×10⁻¹¹ a⁻¹ (Smoliar *et al.*, 1996) of molybdenite reference materials 414 (NISTRM8599 = 27.6 ± 0.1 and 27.6 ± 0.1 Ma; HLP-5 = 220.0 ± 0.9 Ma), which are in 415 good agreement with their accepted values determined at other laboratories and 416 those previously reported at Durham University (Markey *et al.*, 1998, 2007; Porter 417 & Selby, 2010).

418

419 Results

420 The four molybdenite samples from the Loch Shin (n = 1) and Gruide granites (n = 421 3) possess between ~1.6 and 8 ppm Re and 7.5 and 36 ppb 187 Os. All four

422 molybdenite samples yield ages identical within uncertainty (Table II; Figure 10),

423 indicating that mineralization associated with the Loch Shin and the Grudie granite

424 intrusions occurred during the upper mid Silurian (ca. 428 – 430Ma).

425

426 FLUID INCLUSION ANALYSIS

427 Analytical protocols

428 Three molybdenite-bearing quartz veins from the Loch Shin Granite and wall rocks 429 of the Grudie granite were studied in the Geofluids Research Laboratory at the 430 National University of Ireland Galway. A petrographic classification scheme for the 431 quartz-hosted fluid inclusions was developed using transmitted polarised light 432 microscopy (Fig. 11). Microthermometric analysis was performed on doubly 433 polished wafers ($\sim 100 \text{ mm}$ thick) using a Linkam THMGS 600 heating freezing stage, 434 mounted on an Olympus transmitted polarised light microscope. The instrument is 435 equipped with a range of special long working distance objective lenses ranging up 436 to 100x magnification. Calibration of the stage was performed using synthetic fluid 437 inclusion standards (pure CO₂ and H₂O). Precision is \pm 0.5°C at 300°C and \pm 0.2°C at 438 -56.6°C. Following procedures outlined by Shepherd *et al.* (1985), the temperature 439 of first ice melting T_{FM} , the temperature of last ice melting T_{LM} and the temperature 440 of homogenisation T_H were measured in quartz hosted two-phase liquid+vapour 441 inclusions in all wafers (Fig. 12). Fluid salinities were calculated using T_{LM} and the 442 equations of Bodnar (1993). In addition, clathrate melting temperatures recorded in 443 three-phase $(L_{H20}+L_{C02}+V_{C02})$ aqueous-carbonic inclusions were used with the equations of Duan *et al.*, (1996) to calculate their fluid salinities (Fig.12). 444

445 Laser Raman Microspectroscopy (LRM) of fluid inclusions was performed 446 using a Horiba LabRam II laser Raman spectrometer. The instrument is equipped 447 with a 600 groove mm⁻¹ diffraction grating, a confocal and optical filter system, a 448 Peltier-cooled CCD detector (255 x 1024 pixel array), and is coupled to an Olympus 449 BX51 microscope. Fluid inclusion gas and liquid phases were analysed at room 450 temperature using a 532nm laser focused through either a 50x or 100x microscope 451 objectives. The spatial resolution of the 532nm laser at the sample was 452 approximately 2µm. Individual analyses were performed for between 10 to 60 453 seconds over the spectral range 1100 cm⁻¹ to 4200 cm⁻¹. The number of spectral 454 accumulations per analysis typically ranged between 2 to 5 in order to maximize the 455 signal-to-noise efficiency of the spectrometer. Calibration of the instrument was 456 routinely performed between analyses using the Raman peak of a pure silicon 457 standard (520.7 cm⁻¹). Spectral uncertainty associated with the generation of Raman 458 peak positions is estimated to be \pm 1.5 cm⁻¹ (2 σ ; 0.3%) based on replicate analyses 459 of the standard.

460

461 Fluid Inclusion Petrography

Molybdenite-bearing quartz veins were investigated from the Loch Shin Granite (one sample: AF33-10) and from the Moine wall rocks of the Grudie Granite (two samples: AF35-10 and AF02-11). The fluid inclusion petrographic study adopted the concept of fluid inclusion assemblages (FIA) described by Goldstein (2003), an approach that places fluid inclusions into assemblages interpreted to represent contemporaneous fluid trapping. Fluid inclusions (FIs) in all samples display 468 ellipsoidal to irregular morphologies. Inclusions are commonly $\sim 10 \mu m$ in longest 469 dimension and show low degrees of fill (F=0.7-0.95). The degree of fill [F=vol. liquid 470 / (vol. liquid + vol. vapour)] was measured by estimating the proportions of liquid 471 and vapour at 25°C and comparing to published reference charts (Shepherd *et al.*, 472 1985). Four inclusion types (*Type 1, Type 2, Type 3* and *Type 4*) have been identified 473 hosted in vein quartz and their petrological characteristics are presented in Table III. 474 The classification scheme is based on phase relations in fluid inclusions at room 475 temperature. Photomicrographs of fluid inclusion assemblages from each sample 476 are presented in Figure 11 and described below:

477

478 • *Type 1* are two-phase liquid-rich (L>V) aqueous inclusions. They are 479 abundant in all three samples, occurring in trails and in clusters and they 480 commonly display subrounded to irregular shapes. They range from 9 μm to 481 25μ m in length and their degree of fill is ~0.70 to 0.95.

• *Type 2* are monophase aqueous fluid inclusions (L only), and are present in all samples. They occur in trails alongside Type 1 FIs and range in longest dimension from 1 μ m to 5 μ m in length. These are interpreted as being metastable and indicate fluid trapping temperatures of < 50°C (Goldstein and Reynolds, 1994).

Type 3 are three-phase (L+L+V) aqueous-carbonic fluid inclusions. They are
 aligned within annealed fractures and occur as clusters or as isolated
 individuals. They exhibit subrounded to subangular morphologies that range
 between 4 and 17 µm in the longest dimension.

Type 4 are monophase (L) carbonic fluid inclusions. They are aligned within
annealed fractures and also occur in clusters associated with Type 3
aqueous-carbonic inclusions. They range between 5 and 10 µm in longest
dimension and possess rounded to sub-rounded morphologies. They are rare
and have been observed in samples AF33-10 (Loch Shin Granite) and AF0211 (Grudie Granite).

497

498 Fluid Inclusion Microthermometry

In sample AF33-10 from the Loch Shin Granite, T_{FM} values for Type 1 range from -500 50.5° to -45.5°C. This temperature interval indicates the probable presence of NaCl and CaCl₂ (Shepherd *et al.*, 1985). T_{LM} values are from -13.5 to -1.1°C yielding 502 salinities ranging from ~ 1.9 to 17.3 eq. wt. % NaCl (mean 9.7 eq. wt. % NaCl). Fluid 503 inclusions homogenise to the liquid state between 119°-170°C (Table III, Fig. 12 left 504 plot).

505 T_{FM} values for Type 1 in sample AF02-11 from the Grudie Granite wall rocks 506 range between -23° and -22.5°C corresponding to the eutectic point of the H₂O-507 NaCl±KCl system. T_{LM} values range from -3.60 to -0.70°C yielding salinities of ~3.7 508 to 6.9 eq. wt. % NaCl (mean 5.4 eq. wt. % NaCl). Homogenization to the liquid state 509 occurs between 214° and 279°C. In sample AF35-10 T_{LM} values for Type 1 range 510 from -4.3° to -2.2°C yielding salinities ranging from ~1.2 to 5.9 eq. wt. % NaCl (mean 511 4.4 eq. wt. % NaCl) Type 1 FIs homogenise to the liquid state between 151° and 512 244°C (Table III, Fig. 12 left plot).

513 Type 3 aqueous-carbonic inclusions have been identified in all three samples 514 but only microthermometry on Grudie Granite samples (AF02-11 and AF35-10) are 515 reported here, because of the size (<3 microns) of these inclusions in the Loch Shin 516 sample. CO_2 homogenisation (to the liquid state, and by meniscus fading at 31.10°C) 517 occurs between 28° and 30.9°C yielding CO₂ densities that range between 0.47 and 518 0.65 gm/cc. CO₂ melting temperatures range from -56.6°C (the triple point for pure 519 CO_2) to -57.2°C, the latter indicates the presence of additional species (e.g. $H_2S + H_2 -$ 520 see LRM results). Clathrate (CO_2 5.75 HO₂) melting takes place between +5.6° and 521 +9.9°C yielding aqueous phase salinities between ~0.2 and 8.1 eq. wt. % NaCl. Total 522 homogenization to the liquid state occurred between 214.2° and 279.5°C in sample 523 AF35-10, and between 262° and 308.2°C in sample AF02-11. Homogenization to the 524 vapour phase occurred in three inclusions in sample AF02-11 at \sim 332.7°C (Table III, 525 Fig. 12, left plot).

526

527 Laser Raman Microspectroscopy

Laser Raman Microspectroscopy (LRM) was used to identify the phases present in all fluid inclusion types observed in the three samples. LRM revealed the presence of CO₂, N₂ and H₂S (Fig. 13). LRM of Type 1 fluid inclusions in all samples indicates the presence of CO₂. Type 3 FIs from the Grudie granite wall rock samples have in addition to CO₂, trace amounts of H₂S and H₂. LRM of Type 4 FIs from both granites indicates that they are composed of pure CO₂ with trace amounts of H₂S.

534

535 Interpretation

536 The Mo-bearing veins from each of the granites contain a similar range of fluid 537 inclusion types, *i.e.* Types 1-4. Type 1 in the Grudie Granite wall rock veins display 538 similar fluid salinities that range between ~1 and 7 eq. wt. % NaCl. However, Type 1 539 from the Loch Shin Granite, display a significantly wider range of salinities *i.e.* ~2-18 540 eq. wt. % NaCl. This difference is coupled with T_H values for the Loch Shin sample 541 that are generally <180°C which contrasts markedly with the range recorded for 542 Type 1 and 3 from the Grudie Granite wall rock veins (\sim 180°-350°C). T_H histograms 543 (Fig. 12, left plot) for Type 1 and 3 fluid inclusions indicate a decrease in 544 homogenization temperatures from Type 3 (~340°C) through Type 1 (~260°C) in 545 the Grudie Granite wall rock veins to Type 1 (<180°C) fluid inclusions in the Loch 546 Shin Granite vein. Bivariate plots of T_H and salinity show no obvious correlations, 547 however, Type 1 inclusions from the Loch Shin Granite vein display an essentially 548 isobaric variation in salinity (Fig 12, right plot). This low T isobaric trend displayed 549 by the Loch Shin Type 1 inclusions is directly comparable to that displayed by high 550 salinity fluids (Type 3) recorded in the Galway, Donegal, Newry and Leinster 551 Granites in Ireland. Here, they are interpreted to represent basinal brines, sourced 552 in overlying sedimentary basins, which circulated through the crystalline basement 553 during a period of post-Caledonian crustal extension or transtension (see Conliffe 554 and Feely, 2010 and references therein). It is arguable, therefore, that the Type 1 555 fluids recorded in the Loch Shin vein may post-date and be unrelated to Mo-556 mineralisation. Consequently P-T modelling using the fluid inclusion data is only 557 performed for the Grudie Granite veins.

559 P-T Modelling

560 <u>Grudie Granite wall rock veins:</u> The molybdenite Re-Os chronometry shows that the 561 mineralisation in both veins is contemporaneous and occurred ca. 428Ma. 562 Accordingly, the timing of fluid trapping in AF02-11 and AF35-10 is considered to 563 be broadly contemporaneous. Bulk fluid inclusion parameters were calculated using 564 the LRM results in combination with the microthermometric data, using the 565 computer programs CLATHRATES (Bakker, 1997) and FLUIDS (Bakker, 2003).

566 Isochores for the high and lower temperature Type 1 aqueous fluids and for 567 the Type 3 aqueous carbonic fluids in the two vein samples are presented in the P-T 568 diagram (Fig. 14). The field for Type 3 inclusions is defined by two isochores that 569 reflect their range of microthermometric data. Isochores for the lower and higher 570 temperature Type 1 aqueous fluids were constructed for salinities of \sim 4.5 and 5 571 eq.wt% NaCl matched with T_H values of ~176 and ~251°C, respectively 572 corresponding to their range of salinities and T_H values. The veins are spatially and 573 genetically related to the Grudie Granite which places constraints on the pressure 574 regime active during mineralisation. Ferguson and Al-Ameen (1985) calculated 575 pressures of 2.50±0.25kb for the aureole of the Omey Granite, Connemara which has 576 Mo mineralisation of a similar age and setting to the Grudie Granite (Feely *et al.*, 577 2007). These pressure constraints are used in Figure 14 to estimate trapping temperatures for Type 3 fluids of ~340 to 410°C. Furthermore, Gallagher et al., 578 579 (1992) used fluid inclusion microthermometry and stable isotope data to generate a 580 P-T model for Mo- mineralisation at the western end of the Galway Granite which 581 yielded pressures of 1.2 to 2.0kb and a temperature range of 360 to 450°C (see

582 Figure 14). A higher pressure and lower temperature regime prevailed during 583 Grudie Granite mineralisation indeed similar to that modelled for the Omey Granite 584 (Feely et al., 2007). No evidence for fluid immiscibility was recorded in Type 1 585 inclusions and therefore they could have been trapped anywhere along their 586 respective isochores. Type 1 fluids are considered to be meteoric and trapped after 587 and at lower pressures than the earlier magmatic aqueous carbonic Type 3 588 inclusions considered to be responsible for the Mo-mineralisation. The P-T history 589 of fluids in the Grudie Granite wall rock veins may have followed the path shown in 590 Figure 14 (black arrow).

591

592 **DISCUSSION**

593 The relative and absolute ages of plutonism, mineralisation and deformation

594 The U-Pb zircon and Re-Os molybdenite ages for the Loch Shin Granite and sulphide 595 mineralization associated with both plutons are all coincident and overlap almost 596 exactly within error (Fig. 10). These ages therefore confirm the geological 597 observations which suggest that the plutons and associated mineralisation are 598 contemporaneous and genetically related. The Loch Shin-Grudie granite ages 599 overlap within error with the U-Pb zircon (TIMS) age of 425 ± 1.5 Ma reported by 600 Kocks et al. (2013) for the central granodiorite of the Rogart pluton (Fig. 1a) which 601 was, according to these authors also emplaced contemporaneously with dextral 602 movements along the Strath Fleet Fault, the along strike southeastern continuation 603 of the Loch Shin Fault and the LSL (Fig. 1a).

604 The field and thin section observations suggest that the Loch Shin and Grudie 605 granites are petrologically similar – as suggested by previous authors (e.g. Gallagher 606 & Smith 1976). Both plutons post-date the ductile deformation fabrics in the 607 surrounding Moine and Lewisian rocks, including the main Scandian-age D2 608 structures. Both plutons are associated with a variety of ore mineralization, 609 including molybdenite and other base metal sulphides, and both are post-dated by 610 the effects of brittle deformation consistent with dextral transtensional movements 611 along the WNW-ESE-trending Loch Shin Fault. Unsurprisingly the intensity of this 612 brittle overprint is greater in the Loch Shin pluton which lies closer to the main fault 613 trace.

614 The relative ages of the brittle faulting and mineralization are more complex. 615 Field and thin section observations of fracture-hosted sulphides (pyrite, 616 chalcopyrite) show that at least some of the base metal mineralization is 617 contemporaneous with the brittle deformation. This lends support to the long 618 postulated proposal that the dextral movements along NW-SE faults such as the 619 Loch Shin, Strath Fleet and Dornoch Firth fault systems are contemporaneous with, 620 and antithetic to the regional sinistral movements along the Great Glen Fault Zone 621 ca 425 Ma (Johnson & Frost 1977; Watson 1984; Stewart et al. 2001). It also 622 strengthens the arguments made by Dewey & Strachan (2003) and Kocks et al. 623 (2013) that the switch from regional sinistral transpression with thrusting to 624 transtension with regional strike slip faulting occurred at this time.

However, many brittle fractures also cross-cut mineral veins. Furthermore,the Type 1 fluid inclusions seen as Tuttle lamellae in the Loch Shin granite are

627 clearly distinct from the fluid inclusion sets seen in the Grudie granite. Their 628 presence points to a somewhat later, near surface phase of fluid flow associated 629 with brittle dextral movements along the Loch Shin-Strath Fleet Fault system. Given 630 this specific association, it seems most likely that at least some dextral faulting and 631 fluid flow occurred over a protracted period into the Devonian (?Emsian, ca 410 Ma) 632 where it was associated with basin development and the very final stages of late 633 Caledonian strike-slip faulting/transtension (cf. Dewey & Strachan 2003).

634

635 Pluton relationships at depth and the magnitude of dextral strike-slip faulting

636 The very poor levels of exposure in the Loch Shin-Lairg region make it difficult to 637 ascertain how the various plutonic bodies in this area may be related in 3 638 dimensions. Gravity modelling by Hipkin & Hussain (1983) has ruled out the 639 possibility that the large regional gravity low seemingly centred on the surface 640 outcrop of the Grudie pluton (Fig. 1b) is due to the presence of a very large pluton at 641 depth. More recent work by Leslie *et al.* (2010) suggests that the low occurs mainly 642 due to the presence of a thick thrust culmination of Moine rocks (the Cassley 643 Culmination, Fig. 2a) sitting structurally above and to the SE of the Assynt 644 Culmination. Nevertheless, their gravity models suggest the presence of a shallowly 645 buried pluton with horizontal dimensions of 7 x 11 km, with an average thickness of 646 up to 3 km (see Leslie *et al.* 2010, fig. 10). Even allowing for the significant errors in 647 these calculations, this does indicate that the granites exposed in the Loch Shin-648 Lairg region (including the Grudie, Loch Shin, Claonel bodies) are likely to be 649 underlain by a larger, possibly composite plutonic body located mainly to the SW of

650 Loch Shin (Fig. 15a). It is tempting to suggest that this buried granite and the 651 similarly composite Rogart body are part of a single pluton offset by dextral strike-652 slip faulting. However, this would require right lateral displacement of at least 10 653 km which seems at odds with other regional evidence. For example, the observed 654 offsets of regional markers such as the nearby Loch Shin Lewisian inlier (Fig 2a) 655 suggest displacements of no more than a few hundred metres, as does the 656 observation that the Loch Shin Fault does not appear to continue very far to the NW 657 beyond the end of Loch Shin (Leslie et al. 2010). It seems more likely therefore that 658 the two plutons are separate, composite bodies located either side of the Loch Shin-659 Strath Fleet fault system in a manner rather similar to other Caledonian plutons that 660 are associated with regional strike-slip fault zones in NW Scotland, most notably the 661 Great Glen Fault (e.g. Hutton 1988b; Jacques & Reavy 1994; Stewart et al. 2001).

662

663 Implications for the nature and significance of the Loch Shin Line

664 The present study lends support to the suggestion of Watson (1984) that the NW-SE 665 trending Loch Shin Line (LSL) is associated with an anomalous zone of broadly 666 contemporaneous mantle-derived appinites, granites (Rogart, Grudie, Loch Shin and 667 many smaller satellite bodies) intruded ca. 425-428 Ma. These are postdated by 668 slightly younger (perhaps as young as ca 410 Ma) brittle dextral faulting in the 669 Moine Nappe SE of the Moine Thrust (Loch Shin-Strath Fleet and Dornoch Firth 670 faults, Fig. 1b). Watson (1984) suggested that the LSL corresponds to the location of 671 a Precambrian shear zone in the Lewisian autochthon underlying the Moine Nappe 672 which acted as a deep crustal channelway controlling the ascent of magmas and mineralization during the later stages of the Caledonian orogeny (see also the leaky
lower crustal fault block model of Jacques & Reavy 1994). The most obvious
candidate structure seen in the Lewisian Complex west of the Moine Thrust Zone is
the steeply S-dipping Laxford Front, the major shear zone that separates the
Rhiconich and Assynt terranes; this lies almost parallel to and along strike from the
trace of the LSL (Figs 1, 15b).

679

680 *Constraints on regional exhumation rates at the end of the Caledonian orogeny*

681 The PT estimates derived from the fluid inclusion study reported here (Fig. 14) can 682 be compared with those for peak metamorphism in the central part of the foreland-683 propagating Scandian thrust wedge in Sutherland in order to provide constraints on 684 the rate of regional exhumation. Integrated metamorphic and isotopic studies and 685 thermal modelling suggest that peak metamorphic conditions in the vicinity of the 686 Naver Thrust of ca. 650°C and 5.5 kbar (Friend et al. (2000) were attained at c. 440-687 435 Ma (Johnson & Strachan 2006; Thigpen *et al.* 2013). In contrast, this study has 688 established temperature-pressure conditions at the time (ca. 425 Ma) of Grudie 689 Granite mineralisation of c. 375°C and 2.5 kb. The contrasting pressure estimates 690 suggest that around 10 km thickness of crust was removed in c. 10-15 myr, easily 691 achieved at an erosion rate of less than or equal to 1mm ^{a-1}. Essentially the same 692 erosion rate was derived by Johnson & Strachan (2006) from consideration of 693 isotopic data and the likely (Emsian) age of the oldest Old Red Sandstone strata to 694 rest unconformably on the Moine rocks.

696 The regional significance of Caledonian molybdenite mineralization

697 Intrusion-related molydenite mineralization is documented throughout the Scottish 698 and Irish Caledonian-Appalachian Orogen (Figure 1a inset). The broad timing and 699 fluid characteristics of intrusion-related Mo-mineralisation in the Loch Shin and 700 Grudie Granite veins (ca. 428 Ma) is temporally similar to that of the Ballachulish 701 and Kilmelford igneous complexes (ca. 433-426 Ma; Conliffe *et al.*, 2010), pre-dates 702 that of the Etive Igneous Complex (ca. 415 Ma; Porter and Selby, 2010), Shap granite 703 (ca. 405 Ma; Selby *et al.*, 2008) and the earliest granite related Mo-mineralisation in 704 the Irish sector of the Caledonian-Appalachian Orogen (ca. 423Ma, Feely et al., 2010). 705 Fluid inclusion data for these systems indicate that Mo-mineralization is ultimately 706 associated with aqueous-carbonic fluids, which has also been shown to be common 707 among Cu+Mo mineralization associated with late Caledonian magmatism (Kay 708 1985; Gallagher et al. 1992; Feely et al. 2007; Selby et al. 2008; this study; Feely & 709 Selby, unpub data; see Appendix).

710 Gold mineralisation in Dalradian metamorphic rocks at Curraghinalt, 711 Northern Ireland (Parnell et al. 2000; Rice et al., 2012) and Tyndrum, Scotland (Pattrick et al. 1988; Curtis et al. 1993) has also been linked to aqueous-carbonic 712 713 magmatic fluids that may have been derived from an underlying Caledonian 714 intrusive. Although CO₂ has only an indirect role on gold mineralization 715 (Lowenstern 2001), it may play a significant role in magmatic fluid exsolution and 716 evolution, and may lead to concentrations of Au, Cu and Mo into the vapour phase 717 (Heinrich et al. 1999; Ulrich et al. 2001). As such, intrusion-related Mo (+Cu) 718 mineralization may warrant attention during future mineral exploration,

719 particularly for porphyry Cu–Mo-Au mineralization and additionally for 720 structurally-controlled Au-mineralisation distal from the intrusion. In this regard 721 combined fluid inclusion data, U-Pb and Re-Os geochronometry have shown that 722 prolonged granite related molybdenite mineralisation in the Connemara region was 723 accompanied by aqueous-carbonic fluids in the Omey Granite at ca. 423 Ma and later 724 in the Galway Granite at ca. 410Ma (Murvey), ca. 407Ma (Mace Head) and ca. 380Ma 725 (Costelloe; Feely et al., 2007, 2010). Moreover, the earliest granite related Mo-726 mineralisation of the Omey Granite was also initiated while major orogen parallel 727 structures, e.g. Great Glen and Southern Upland Fault systems (Dewey and Strachan, 728 2003) were active.

729

730 CONCLUSIONS

731 Using detailed field observations, microstructural studies, U-Pb zircon and Re-Os 732 molybdenite geochronology and fluid inclusion analyses, we have shown that a suite 733 of mid-Silurian (ca. 425-430 Ma) granite plutons (Grudie, Loch Shin, Rogart and 734 many smaller associated bodies) are contemporaneous with base metal sulphide 735 mineralization, including molybdenite. Synchronous to slightly younger (ca. 427-736 410Ma) brittle dextral strike slip faulting along the WNW-ESE Loch Shin-Strath 737 Fleet Fault System was antithetic to regional sinistral strike-slip movements along 738 the NE-SW trending Great Glen Fault (Fig. 15a). More generally, the associated 739 plutonism, mineralization and strike-slip faulting confirms the transition from 740 regional-scale transpression to transtension during the mid-Silurian to early 741 Devonian in NW Scotland as postulated by Dewey & Strachan (2003).

742 Our findings also lend support to the existence of the NW-SE trending Loch 743 Shin Line and to the hypothesis of Watson (1984) that it has acted as a deep crustal 744 channelway controlling the ascent and emplacement of Silurian granitic and 745 appinitic magmas into the overlying Moine Nappe (Fig. 15b). It seems very likely 746 that this deep structure corresponds to the southeastern continuation of the 747 Precambrian-age Laxford Front shear zone in the buried Lewisian autochthon. This further illustrates how pre-existing crustal structures can be persistently 748 749 reactivated even when buried beneath much younger thrust nappes and influence 750 directly the migration and emplacement of hydrous mineralizing fluids and magmas 751 (e.g. Jacques & Reavy 1994; Richards 2013).

752

753 Acknowledgements

To be added

755

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- 994

995 Figure captions

Figure 1a) Regional geology map of the northern Scottish Highlands. Inset map
shows the relative positions of Laurentia, Baltica, Avalonia and Gondwana following
the closure of the Iapetus Ocean (Caledonide-Appalachian belt in black).
Abbreviations as follows: A = Assynt; DFF = Dornoch Firth Fault; GGF = Great Glen
Fault; LCM = Loch Coire Migmatite complex; LSSFF = Loch Shin - Strath Fleet Fault ;
MF = Moray Firth; MT = Moine Thrust; NT = Naver Thrust; ORS = Old Red
Sandstone; R = Rogart igneous complex.

- b) Gravity map of the Lairg-Loch Shin area, with locations of appinnitic intrusions
 (Achnuie hybrids), Laxford front and surface trace of Loch Shin Line shown (after
 Watson 1984 and Leslie *et al.* 2010).
- 1006

Figure 2a) Overview geological map of the Loch Shin area after Strachan and
Holdsworth (1988) & Leslie *et al.* (2010). Box shows location of map shown in
Figure 2b. G= Grudie, C = Claonel, LS = Loch Shin granites. L = Lairg; LSF = Loch Shin
Fault; AS = Aird of Shin. b) Simplified version of geology in the Loch Shin – Grudie
area (after Gallagher & Smith 1976). Geochronology sample locations are shown. GB
Grudie Burn; CCB = Cnoc na Cloich-bhuaile; MG = Meall a'Ghruididh; AC = Allt
a'Chlaonaidh.

1015 Figure 3) The country rocks, Loch Shin granite and associated veins viewed in the 1016 field and thin section. a) Oblique view looking down onto undeformed granite 1017 pegmatite vein (077/55 NNW) cutting ACW of compositional banding in Moine 1018 psammites (100 metres to the SE of the Loch Shin granite (NC 5639 0613). Arrow 1019 shows inferred direction of vein opening based on offsets of thin semipelite layer. **b**) 1020 Thin section of undeformed granite pegmatite vein shown in (a) cross-cutting SO-1021 S1-S2 fabric in Moine psammites (dashed vellow line). View in crossed polars, with 1022 igneous contact shown in red. c) Plan view in the field (NC 5631 0650) and d) in 1023 thin section (crossed polars) of typical undeformed Loch Shin granite (NC 5635 1024 0631). e) Close-up plan view of irregular quartz-pyrite veins cutting Loch Shin 1025 granite (NC 5631 0650). f) Cross-section view of large NW-SE-trending quartz-1026 galena veins (107/85N) cutting Loch Shin granite (NC 5630 0659).

1027

1028 Figure 4) Equal area stereoplots of structural data collected from the Loch Shin 1029 shore section. a) Ductile foliation (Sn/S2; great circles) and L2 mineral lineations 1030 (dots). **b)** Granite veins (red, great circles) and quartz veins (green, great circles) 1031 and lineation on quartz vein (dot). c) Steep faults (great circles) and slickenlines 1032 (dots). d) Shallow faults (great circles) and slickenlines (dots). e) Box fold hinges 1033 (dots) and axial surfaces (great circles). f) Stress inversion analysis and Mohr plot of 1034 combined fault slickenline data with weighting added to include fault sizes. LSF = 1035 inferred local orientation of Loch Shin Fault.

1036

1037 Figure 5) Brittle structures cutting the Loch Shin granite and its Moine country

1038 rocks. a) Plan view of NE-SW sinistral fault offsetting granite and quartz vein (NC 1039 5635 0631). **b)** Plan view of NW-SE dextral fault offsetting granite pegmatite vein in 1040 Moine psammites (NC 5639 0613). c) Oblique sectional view of long NW-SE 1041 trending dextral fault scarp in Loch Shin granite; inset shows sub-horizontal 1042 orientation of slickenlines on fault surface consistent with strike-slip fault 1043 movement (NC 5631 0650). d) NE-SW sinistral fault offsetting and being offset by 1044 NNW-SSE dextral faults in Loch Shin granite (NC 5635 0631). e) Shallowly NW-1045 dipping flats and shorter SE-dipping ramps ('r') in exposed small displacement, top-1046 to-the-NW faults; inset shows plan view of corrugated, lineated fault surface with NW-SE slickenlines (NC 5635 0632). **f**) Plan view of steeply plunging conjugate box 1047 1048 folds detaching along sub-vertical NE-SW sinistral fault in Moine psammites (NC 1049 5638 0621).

1050

1051 Figure 6) Thin sections of brittle structures and mineralization cutting the Loch 1052 Shin granite and its country rocks. **a)** Small offset (<0.5mm) domino style reverse 1053 (top-to-the-NW) shear fractures (arrowed) cutting Loch Shin granite viewed in ppl 1054 (NC 5635 0632). **b)** Typical zone of cataclasis cross cutting Loch Shin Granite 1055 viewed in crossed polars (NC 5635 0632). c) Irregular region of quartz iron oxide-1056 ilmenite (black) -pyrite (black, Py) –fluorite (Fl) mineralization in Moine psammites 1057 immediately to the northwest of the Loch Shin granite viewed in ppl (NC 5625 1058 0666). d) Multiple sets of fluid inclusions following healed microcracks/Tuttle 1059 lamellae in quartz from the Loch Shin granite viewed in ppl (NC 5635 0632). e) 1060 Microfactures lined with sericite where they cross-cut feldspar (Fsp) passing 1061 laterally into healed microcracks/Tuttle lamellae in quartz (Qtz), in granite
1062 pegmatite vein, viewed in crossed polars (NC 5639 0613). f) Late zeolite vein (Z)
1063 cutting brecciated Moine psammite viewed in cross-polars (NC 5625 0666).

1064

1065 Figure 7) Field and thin section views of the Grudie granite. a) Plan view of typical 1066 unfoliated Grudie granite with large pink K-feldspar and grey quartz 1067 phenocrysts/xenocrysts (NC 5268 0450). b) Oblique section view of slickenlined 1068 joints with chlorite and epidote mineralization (NC 5267 0444). c) Thin section of 1069 typical K-feldspar (in extinction) and d) polycrystalline quartz 1070 xenocryst/phenocrysts within Grudie granite (NC 5310 0427).

1071

Figure 8) Plot of the U-Pb zircon and Re-Os molybdenite dates including 2 sigma
uncertainty with decay constant uncertainty for the Loch Shin and Gruide granites.
Also given is the weighted average for the Re-Os molybdenite dates for the Gruide
granite. For sample locations, see Figure 2.

1076

Figure 9) Cathodoluminescence images and SHRIMP II analysis positions for representative grains from grains selected for geochronology from the Loch Shin Granite sample. Also shown are the grain numbers, and 207Pb/206Pb ages for each analysis pit (uncertainties are two standard deviations; percentage discordance shown in brackets).

1082

1083 **Figure 10 a, b)** Zircon U-Pb concordia plots from the Loch Shin granite.

1084

Figure 11) Photographs of fluid inclusions (FI) trails from samples AF33-10 – Loch
Shin Granite (a,b); AF35-10 (c,d) and AF02-10 (e,f) both from Gruide Granite. Scale
bar = 50 μm.

1088

Figure 12) Histogram of TH values (a) and bivariate plot of TH vs. salinity (b) for
Type 1 and Type 3 inclusions in samples AF02-11 and AF35-10 from the Gruide
granite and for Type 1 in sample AF33-10 from the Loch Shin granite.

1092

Figure 13) Photomicrographs of Type 1 and Type 3 inclusions within quartz grains
in sample AF35-10 (Gruide granite) analysed under Laser Raman Spectroscopy.
Type 1 two-phase liquid-rich aqueous inclusions distributed in isolated cluster (a)
and trails (b). Type 3 three-phase aqueous-carbonic inclusions distributed in
clusters (c and d).

1098

1099 **Figure 14)** Pressure-temperature space showing isochores for Type 1 and Type 3 1100 fluid inclusions. Shaded area represents the field for Type 3 fluids defined by two 1101 isochores. Isochores for the lower and higher temperature Type 1 aqueous fluids 1102 are also shown and the parameters used for their construction are shown on the 1103 isochores. Proposed *P-T* path for cooling history of fluids in Grudie Granite is shown 1104 by the arrow. *P*-*T* field for aqueous carbonic fluids associated with the Mo 1105 mineralisation at the western end of the Galway Granite is shown for comparison 1106 after Gallagher *et al.*, (1992).

Figure 15) a) 3-D summary of the spatial relationships between the Rogart, Loch
Shin, Lairg and Grudie plutons (red) and brittle strike slip faults (grey) in the Loch
Shin-Strath Fleet-Dornoch Firth area. b) Highly simplified conceptual model
showing how the buried Laxford front shear zone below the Moine nappe gives rise
to the Loch Shin Line of focussed Silurian magmas and overlapping dextral strike-
slip faults.
Tables
Table I) U-Pb data for Loch Shin granite.
Table II) Re-Os data for molybdenite from the Loch Shin and Gruide granites.
Table III) Classification of fluid inclusion types and fluid inclusion micro-
thermometric data from the Loch Shin and Gruide granites.































School of	Earth and Environme	ntal Sciences,	Univers	ity of Ports	mouth	١		Data for Te	ra-Was	serburg plot	2	
Identifier	Comments	Beam (µm) L	J (ppm)1	Th (ppm)1	Th/U	²⁰⁶ Pb/ ²⁰⁴ Pb	1s%	²³⁸ U/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁷ Pb/ ²³⁵ U
Sample DS	S1-11											
DE10A05		25x37	254	112	0.44	3925	37	3.494	0.039	0.106	0.001	4.188
DE10A06		25x37	208	92	0.44	2414	32	3.251	0.038	0.107	0.001	4.716
DE10A07		25x37	241	267	1.11	971	22	14.451	0.172	0.055	0.001	0.536
DE10A08		25x37	335	384	1.15	1722	37	14.558	0.258	0.056	0.001	0.523
DE10A09		25x37	105	61	0.58	2739	37	3.222	0.041	0.108	0.001	4.775
DE10A11		25x37	465	481	1.03	505	40	14.738	0.235	0.056	0.001	0.541
DE10A12		25x37	266	228	0.85	891	30	14.558	0.166	0.055	0.001	0.521
DE10A13	High 204Pb - rejected	25x37	105	161	1.54	316	32	14.490	0.197	0.071	0.002	0.695
DE10A14		25x37	51	30	0.59	790	30	4.452	0.070	0.084	0.001	2.662
DE10A15		25x37	141	154	1.1	348	27	15.079	0.188	0.056	0.001	0.506
DE10A16		25x37	282	259	0.92	1135	27	14.817	0.332	0.055	0.001	0.527
DE10B05		15x27	220	412	1.87	1814	30	14.974	0.322	0.056	0.002	0.522
DE10B06	High 204Pb - rejected	15x27	538	690	1.28	566	34	14.391	0.238	0.080	0.002	0.769
DE10B07		15x27	253	209	0.83	1225	28	13.377	0.211	0.059	0.001	0.634
DE10B08		15x27	64	77	1.19	399	30	14.353	0.260	0.055	0.002	0.518
DE10B09		15x27	123	187	1.52	615	49	14.502	0.214	0.055	0.001	0.521
DE10B10		15x27	144	191	1.33	583	33	14.305	0.193	0.056	0.001	0.539
DE10B11		15x27	290	403	1.39	1043	27	13.439	0.219	0.061	0.001	0.628
DE10B12	High 204Pb - rejected	15x27	674	1044	1.55	242	31	16.761	0.403	0.124	0.008	0.930
Standard	GJ-1											
DE10AA04	Ļ	30x45	389	26	0.04	1301	26	10.158	0.095	0.060	0.001	0.807
DE10AA12	2	30x45	266	11	0.04	1245	28	10.125	0.091	0.060	0.001	0.821
DE10AA17	,	30x45	310	9	0	1178	28	10.127	0.143	0.060	0.001	0.818
DE10A04		30x45	300	13	0.04	1306	27	10.133	0.086	0.060	0.001	0.828
DE10A10		30x45	292	13	0.04	1205	27	10.151	0.087	0.060	0.001	0.826
DE10A17		30x45	289	12	0.04	1441	36	10.161	0.097	0.060	0.001	0.822

DE10B04	30x45	270	12	0.04	1176	42	10.155 0.118	0.060 0.001	0.831
DE10B13	30x45	267	11	0.04	965	34	10.179 0.120	0.059 0.001	0.814
Standard Temora 2									
DE10AA05	30x45	141	83	0.6	1043	30	15.103 0.234	0.055 0.001	0.509
DE10AA06	30x45	143	85	0.6	1313	23	14.686 0.180	0.055 0.001	0.518
DE10AA07	30x45	145	86	0.6	1067	36	14.767 0.181	0.055 0.001	0.514
DE10AA08	30x45	144	100	0.7	1122	31	14.805 0.189	0.055 0.001	0.511
DE10C05	30x45	373	205	0.5	845	28	14.813 0.194	0.055 0.001	0.504
DE10C06	30x45	327	193	0.6	1187	34	14.974 0.206	0.055 0.001	0.498
De10C14	20x30	346	188	0.5	1042	34	15.231 0.177	0.055 0.001	0.504
De10C15	20x30	292	163	0.6	1063	29	15.126 0.180	0.055 0.001	0.501

1 concentration uncertainty c.20%

2 data not corrected for common-Pb

3 Concordance calculated as (206Pb-238U age/207Pb-206Pb age)*100

Decay constants of Jaffey et al 1971 used

Data fo	or Wetherill p	lot2				Ages2				
1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	Rho	²⁰⁷ Pb/ ²⁰⁶ Pb	1σ	²⁰⁶ Pb/ ²³⁸ U	1σ	²⁰⁷ Pb/ ²³⁵ U	1σ	% conc5
					abs		abs		abs	
0.061	0.286	0.003	0.8	1725	16	1622	18	1672	25	94
0.070	0.308	0.004	0.8	1742	16	1729	20	1770	26	99
0.012	0.069	0.001	0.5	431	8	431	5	436	10	100
0.012	0.069	0.001	0.6	435	8	428	8	427	10	99
0.093	0.310	0.004	0.9	1771	18	1743	22	1780	35	98
0.011	0.068	0.001	0.5	444	8	423	7	439	9	95
0.010	0.069	0.001	0.6	427	6	428	5	426	8	100
0.023	0.069	0.001	0.8	945	22	430	6	536	18	46
0.065	0.225	0.004	0.8	1285	19	1306	21	1318	32	102
0.012	0.066	0.001	0.6	454	9	414	5	416	10	91
0.019	0.067	0.002	0.8	432	9	421	9	430	15	97
0.013	0.067	0.001	0.2	446	13	417	9	426	11	93
0.020	0.069	0.001	0.3	1209	32	433	7	579	15	36
0.012	0.075	0.001	0.6	572	9	465	7	499	10	81
0.022	0.070	0.001	0.5	429	16	434	8	424	18	101
0.015	0.069	0.001	0.6	409	10	430	6	426	13	105
0.012	0.070	0.001	0.5	436	9	436	6	438	10	100
0.014	0.074	0.001	0.5	638	13	463	8	495	11	73
0.041	0.060	0.001	-0.9	2021	134	374	9	667	30	18
0.011	0.098	0.001	0.3	594	8	605	6	601	9	102
0.014	0.099	0.001	0.4	605	9	607	5	609	11	100
0.012	0.099	0.001	0.7	609	7	607	9	607	9	100
0.011	0.099	0.001	0.6	602	6	607	5	613	8	101
0.011	0.099	0.001	0.7	613	6	606	5	611	8	99
0.012	0.098	0.001	0.7	600	7	605	6	609	9	101

0.01	3 0.098	0.001	0.7	590	7	605	7	614	10	103
0.01	3 0.098	0.001	0.7	580	7	604	7	605	10	104
					_		-			
0.01	0 0.066	0.001	0.4	429	9	413	6	418	8	96
0.01	0.068	0.001	0.4	415	8	425	5	424	8	102
0.01	0.068	0.001	0.4	426	8	422	5	421	8	99
0.01	0.068	0.001	0.4	427	8	421	5	419	8	99
0.00	9 0.068	0.001	0.7	417	6	421	6	415	8	101
0.00	9 0.067	0.001	0.7	411	6	417	6	410	7	101
0.00	9 0.066	0.001	0.7	416	6	410	5	414	8	98
0.00	9 0.066	0.001	0.6	414	6	413	5	413	7	100
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Table II.

Sample	Location	wt	Re (ppm)	±	¹⁸⁷ Re (ppm)	±	¹⁸⁷ Os (ppb)	±	Age (Ma)	±	± (λ ¹⁸⁷ Re uncert)
Loch Shin											
AF33-10	Loch Shin, NC 56139, 06495	0.021	1.67	0.01	1.05	0.01	7.5	0.0	427.9	2.8	3.1
Gruide Granite											
AF36-10	Moly Burn (Gallagher & Smith, 1975), NC 51530, 04646	0.012	3.53	0.03	2.22	0.02	15.9	0.1	429.6	5.2	5.6
AF01-11	Edge of Grudie Granite NC 52726, 03797	0.014	3.40	0.03	2.14	0.02	15.4	0.1	429.9	5.2	5.6
AF02-11	Edge of Grudie Granite NC 52726, 03797	0.010	8.04	0.05	5.05	0.03	36.1	0.2	428.0	3.0	3.3

Fluid Inclusion Types	Loch Shin granite	Gruide granite				
	sample AF33-10	sample AF35-10	sample AF02-11			
Type 1 two-phase (L+V) liquid-rich aqueous inclusions 9-25 μm; sub-rounded and irregular shapes; occurr in trails aligned within annealed fractures; some clusters ¹ fluid composition: H ₂ O-NaCl±KCl±CO ₂	F: 0.85-0.9 T_{FM} : -45.5° to -50.5° (mean: -47.9°C; N=7) T_{LM} : -13.5° to -1.1° (mean: -6.9°C; N=17) Salinity: 1.9 to 17.3 eq. wt%NaCl (mean: 9.7; N=17) $T_{H}\rightarrow$ L: 119° to 170.1° (mean: 152.9°C; N=20) Abundant	F: 0.8-0.95 T_{LM} : -3.6° to -0.7° (mean: -2.8°C; N=20) Salinity: 1.2 to 5.9 eq. wt%NaCl (mean: 4.4; N=20) $T_{H}\rightarrow$ L: 151° to 244.4° (mean: 185.6°C; N=20) Abundant	F: 0.7-0.9 T_{FM} : -22.5° to -23° (mean: -22.8°C; N=2) T_{LM} : -4.3° to -2.2° (mean: -3.3°C; N=20) Salinity: 3.7 to 6.9 eq. wt%NaCl (mean: 5.4; N=20) $T_{H}\rightarrow$ L: 214.2° to 279.5° (mean: 258.3°C; N=20) Abundant			
Type 2 monophase (L) liquid aqueous inclusions 1-5 μm; rounded to sub-rounded shapes; occurr in trails within annealed fractures and randomly distributed fluid composition: H ₂ O-NaCl	² Trapping T < 50°C Abundant	Trapping T < 50°C Abundant	Trapping T < 50°C Abundant			
Type 3 three- phase (L+L+V) aqueous-carbonic inclusions 4-17 μm; elongated and irregular shapes; occurr in trails aligned within annealed fractures; isolated or in clusters fluid composition: H ₂ O-CO ₂ .NaCl±H ₂ S±H ₂	F: 0.8-0.9	F: 0.8-0.9 T_{MCO2} : -57.1° to -56.5° (mean: -56.7°C; N=20) T_{Mclath} : 7.2° to 8.2° (mean: 8°C; N=18) T_{HCO2} → fading: 30.5° to 31.1° (mean: 30.8°; N=20) Salinity: 3.6 to 5.4 eq. wt%NaCl (mean: 4; N=18) Density: 0.468 g/cm ³ T_{HTOT} →L: 228.2° to 261° (mean: 243.5°C; N=20) Abundant	F: 0.4-0.85 T_{MCO2} : -57.2° to -56.2° (mean: -56.7°C; N=17) T_{Mclath} : 5.6° to 9.9° (mean: 7.2°C; N=19) $T_{HCO2} \rightarrow L$: 28° to 30.9°; $T_{HCO2} \rightarrow$ fading 31.1° Salinity: 0.2 to 8.1 eq. wt%NaCl (mean: 4.4; N=19) Density: 0.468 to 0.655 g/cm ³ $T_{HTOT} \rightarrow L$: 262° to 312.5° (mean: 243.5°C; N=10) $T_{HTOT} \rightarrow V$: 305° to 348° (mean: 332.7°C; N=3)			
Type 4 monophase (L) carbonic inclusions 5-10 μm; rounded to sub-rounded shapes; occurr in trails aligned within annealed fractures; some isolated fluid composition: CO ₂ ±H ₂ S	Rare	Not Observed	Rare			

Classification is based upon FI morphology and the volumetric proportion of phases observed at room temperature. L = liquid, V = vapour. ¹Bulk composition based on combined microthermometry and Raman spectroscopy. ²The presence of monophase aqueous liquid FIs indicate trapping temperatures of < 50°C⁻ ± : trace or minor constituent. T_{FM} : temperature of first ice melting; T_{LM} : temperature of last ice melting; $T_{HTOT} \rightarrow L$: homogenisation temperature of clathrate melting; F: degree of fill; F=vol. liquid / (vol. liquid+vol. vapour).