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A review of molybdenite, and fluorite mineralization in Caledonian granite basement, western Ireland, incorporating new field and fluid inclusion studies, and Re-Os and U-Pb geochronology.

Martin Feely[1]*, Alessandra Costanzo[1], Sean P. Gaynor[2,3], David Selby[4] and Emma McNulty[1]

[1] Geofluids Research Group, Earth and Ocean Sciences, School of Natural Sciences, National University of Ireland Galway, Galway, Ireland
[2] Department, of Geological Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, 27510, USA
[3] *Now at* Department of Earth Sciences, University of Geneva, rue des Maraîchers 13, Geneva, Switzerland
[4] Department of Earth Sciences, Durham University, Durham, UK

Abstract

The recent discovery of late-magmatic quartz vein hosted molybdenite, and exceptional gem quality vein fluorite, in the Caledonian Galway Granite Complex (GGC), has prompted a review of these contrasting styles of mineralisation in the late-Caledonian granite basement, Connemara, western Ireland. Existing published U-Pb and Re-Os chronometry and fluid inclusion microthermometry are combined with new: a) geological field observations, b) U-Pb zircon and Re-Os molybdenite geochronometry and c) fluid inclusion microthermometry to generate a new pressure-temperature-time model (P-T-t) of mineralization for the GGC. Re-Os chronometry molybdenite indicates that granite related molybdenite mineralisation extended from ~423Ma to ~380Ma overlapping with the GGC emplacement history determined by U-Pb zircon chronometry. The P-T-t model reflects initial granite emplacement and Mo-mineralisation at ~423Ma followed by lower P and T granite emplacement and related quartz vein hosted Mo-mineralisation at ~410Ma (Carna pluton), ~400Ma (Kilkieran pluton) and at ~380Ma (Costelloe Murvey granite). The gem quality fluorite veins in the GGC represent late-Triassic hydrothermal mineralisation that forms part of a regional N Atlantic-European Triassic-Jurassic hydrothermal mineralisation province triggered by the rifting of the N Atlantic facilitating crustal thinning and subsidence of

continental crust and initiating hydrothermal activity at the margins of Mesozoic basins thus

facilitating hydrothermal vein fluorite mineralisation in, for example, the Caledonian GGC of

western Ireland.

1 **A review of molybdenite, and fluorite mineralization in Caledonian**
2 **granite basement, western Ireland, incorporating new field and fluid**
3 **inclusion studies, and Re-Os and U-Pb geochronology.**
4

5 Martin Feely[1]*, Alessandra Costanzo[1], Sean P. Gaynor[2,3], David Selby[4,5] and Emma
6 McNulty[1]
7

8 [1]Geofluids Research Group, Earth and Ocean Sciences, School of Natural Sciences,
9 National University of Ireland Galway, Galway, Ireland
10 [2]Department, of Geological Sciences, University of North Carolina at Chapel Hill,
11 Chapel Hill, North Carolina, 27510, USA
12 [3]*Now at* Department of Earth Sciences, University of Geneva, rue des Maraîchers 13,
13 Geneva, Switzerland
14 [4]Department of Earth Sciences, Durham University, Durham, UK

15 [5] State Key Laboratory of Geological Processes and Mineral Resources, School of
16 Earth Resources, China University of Geosciences, Wuhan, 430074, China
17

18 **Abstract**

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20 exceptional gem quality vein fluorite, in the Caledonian Galway Granite Complex

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22 Caledonian granite basement, Connemara, western Ireland. Existing published U-Pb

23 and Re-Os chronometry and fluid inclusion microthermometry are combined with

24 new: a) geological field observations, b) U-Pb zircon and Re-Os molybdenite

25 geochronometry and c) fluid inclusion microthermometry to generate a new pressure-

26 temperature-time model (P-T-t) of mineralization for the GGC. Re-Os chronometry

27 molybdenite indicates that granite related molybdenite mineralisation extended from

28 423 to 380Ma overlapping with the GGC emplacement history determined by U-Pb

29 zircon chronometry. The P-T-t model reflects initial granite emplacement and Mo-

30 mineralisation at ~423Ma followed by lower P and T granite emplacement and related

31 quartz vein hosted Mo-mineralisation at ~410Ma (Carna pluton), ~400Ma (Kilkieran

32 pluton) and at ~380Ma (Costelloe Murvey granite). The gem quality fluorite veins in

33 the GGC represent late-Triassic hydrothermal mineralisation. These veins form part

34   of a regional N Atlantic-European Triassic-Jurassic hydrothermal mineralisation

35   province. Vein emplacement was triggered by the rifting of the N Atlantic facilitating

36   crustal thinning and subsidence of continental crust and initiating hydrothermal

37   activity at the margins of Mesozoic basins.

38

39   **Keywords:** Caledonian granite basement, late-magmatic molybdenite, Triassic

40   hydrothermal fluorite

41

42   **Introduction**

43   One of the most significant and economically important types of mineralising fluid

44   flow regimes in the crust are those related to granitic intrusions. Molybdenite

45   mineralisation for example, is genetically related to granite magmatism. The

46   Caledonian-Appalachian Orogen is marked by a ~50 m.y. period of granite intrusions

47   with associated molybdenite mineralisation systems (**Ayuso, 1999; Plant, 1986;**

48   **Whalen, 1993; Lynch et al. 2009**). Furthermore, granitic basement rocks invariably

49   contain a variety of economic and sub-economic mineral and hydrocarbon deposits

50   that postdate the crystalline host. Global occurrences of younger hydrothermal vein

51   mineralising systems are well documented (*e.g.* **Chesley *et al.,* 1993; Munoz *et al.,***

52   **1994; Halliday and Mitchell, 1984; Canals and Cardellach, 1993; McCaffrey *et***

53   ***al.,* 1999; Conliffe and Feely, 2010**), as are biogenic hydrocarbons in fractured

54   granitic and other crystalline basement rocks (**Parnell, 1988; Petford and**

55   **McCaffrey, 2003; Trice, 2014; Feely *et al.*, 2017; Holdsworth *et al.,* 2019**).

56   The recent discovery of quartz vein hosted molybdenite, and exceptional gem quality

57   vein fluorite, in a working quarry (Larkin's Connemara Granite Quarry,

58   Shannapheasteen), has prompted a re-investigation of these contrasting styles of

59 mineralisation in the late-Caledonian GGC of south Connemara. This quarry, like the

60 one described by **O'Connor *et al.,* (1993**), also exposes a mid-Palaeozoic dike that is

61 cut by millimetric scale veinlets of fluorite. Accordingly, existing published U-Pb and

62 Re-Os chronometry and fluid inclusion microthermometry are combined with new

63 geological field observations, U-Pb zircon and Re-Os molybdenite geochronometry

64 and fluid inclusion microthermometry to generate a new P-T-t (Pressure-

65 Temperature-time) regional scale model of late-magmatic Mo-mineralization and later

66 hydrothermal fluorite mineralisation in the GGC.

67 The new data presented here provides supporting evidence for prolonged and episodic

68 granite emplacement in tandem with granite related molybdenite mineralisation in the

69 GGC and in other granites along the Caledonian-Appalachian orogen (Feely et al.

70 2010). The molybdenite in the GGC is an integral part of the granite related

71 molybdenite mineralization corridor located along the Caledonian-Appalachian

72 orogeny of the North Atlantic Massif. The fluorite mineralization in the GGC is

73 broadly synchronous with other Triassic-Jurassic hydrothermal vein mineralisation

74 throughout the North Atlantic margins and Europe and forms part of a hydrothermal

75 province identified by Mitchell and Halliday (1976).

76

77 **Regional Setting of the Galway Granite Complex**

78 The GGC occupies a key location in the Appalachian-Caledonian orogenic belt. The

79 80 km long, WNW-trending axis of the GGC lies astride and stitches the EW-trending

80 Skird Rocks Fault, a splay of the orogen-parallel Southern Uplands Fault (**Leake,**

81 **2006**). The Skird Rocks Fault brings amphibolite facies rocks of the Grampian

82 Connemara Metamorphic Complex against the Lower Ordovician greenschist-facies

83 rocks of the South Connemara Group. The Connemara Metamorphic Complex

84 comprises Lower to Upper Dalradian greenschist to amphibolite facies rocks, intruded

85 by a) the Grampian phase 470–465Ma Metagabbro-Gneiss Suite, then by b) the

86 Oughterard Granite (~463Ma) and c) the Silurian-Devonian GGC (~425–380Ma)

87 (**Leake, 1989; Leake and Tanner, 1994; Friedrich *et al*., 1999a, b; Pracht *et al*.,**

88 **2004; Feely *et al.,* 2006; Leake, 2006; Feely *et al.,* 2010; Dewey and Ryan, 2016;**

89 **Friedrich and Hodges, 2016; Feely *et al.,* 2018).** In the north, the Dalradian

90 metasediments are overlain by Silurian strata (**Leake and Tanner, 1994**) and in the

91 south Lower Ordovician greenschist facies rocks (the South Connemara Group) are

92 intruded by the GGC (**McKie and Burke, 1955; Williams *et al.,* 1988**). The Delaney

93 Dome Formation, is a 474.6 ± 5.5 Ma metavolcanic complex (**Leake and Singh,**

94 **1986; Draut and Clift, 2002**). To the east the metamorphic and igneous rocks of the

95 Connemara region are in faulted contact with Carboniferous Limestones (**Lees and**

96 **Feely, 2016 and 2017**) - see **Figure 1.**

97

98 **Molybdenite, and fluorite mineralisation in the GGC-a research history**

99 The well-exposed Silurian-Devonian GGC provides a unique opportunity to study the

100 temporal and spatial relationships of late-magmatic Mo-mineralisation (with

101 associated chalcopyrite), and the later hydrothermal fluorite veins that can include

102 varying proportions of galena, sphalerite, chalcopyrite/pyrite, calcite, barite and

103 quartz. Indeed, numerous studies of the spatial distribution and structural controls of

104 the Mo-mineralisation in the GGC were published in the late 20th Century *e.g*.,

105 **Derham (1986); Max and Talbot (1986); Derham and Feely (1988); McCaffrey *et***

106 ***al.* (1993)**. In addition, fluid inclusion microthermometry combined with stable

107 isotope studies (O, H, S, C) were used to investigate the genesis of the Mo-

108 mineralisation (**Feely and Hoegelsberger, 1991; Gallagher *et al.,* 1992; O'Reilly *et***

109 *al.,* **1997**). The results of a regional fluid inclusion study by **O'Reilly** *et al.* **(1997)** and

110 later supported by **Feely** *et al.***, (2007)**, show that late-magmatic, high-T (~450°C) low

111 to moderate salinity (4–10 eq. wt% NaCl) aqueous-carbonic fluids were associated

112 with the Mo-mineralisation. A second, aqueous fluid, of lower–T (~270–340°C) and

113 low to moderate salinity (0–10 eq. wt.% NaCl) is ubiquitous throughout granite and

114 vein quartz in the GGC and is interpreted to reflect mixing between late magmatic and

115 meteoric fluids. Finally, microthermometry shows that fluid inclusions associated

116 with the fluorite mineralization veins are $CaCl_2$ bearing and more saline (8–28 eq.

117 wt.% NaCl) and have lower temperatures (~125–205°C) than the earlier fluids.

118 Furthermore, **Jenkin** *et al.* **(1997)** noted that pressures during the deposition of these

119 late-Triassic fluorite veins were <0.7 kb. **Conliffe and Feely (2010)** in their regional

120 study of fluid inclusions hosted by granite quartz in onshore Irish granite basement

121 recorded the presence of these fluids, arguing that they represent mixing between

122 meteoric and basinal fluids probably of Carbonifeous to Triassic in age. It is also

123 noteworthy that **Conliffe** *et al.***, (2010)** described similar fluids in sandstones from

124 offshore Irish Mesozoic basins.

125 Many of the early fluid inclusion studies were based upon the assumption that the

126 whole of the GGC was ~400Ma in age and that therefore the Mo-mineralization was

127 also ~400Ma in age. **Leake and Tanner (1994)** for example, observed that the whole

128 suite of plutons making up the GGC were late Caledonian and approximately 400Ma

129 old. New geochronology studies, using the U-Pb zircon and Re-Os molybdenite

130 chronometers have shown that the assembly of the GGC involved five main magmatic

131 episodes extending from 423 to 380Ma (**Buchwaldt** *et al.,* **2001; Feely** *et al,.* **2003;**

132 **Selby** *et al.,* **2004; Feely** *et al.,* **2007; Feely** *et al.,* **2010; Feely** *et al.,* **2018**). The

133 earliest magmatic episode ~423Ma was marked by the emplacement of the Omey,

134   Inish and Roundstone Plutons. These were followed by the Carna Pluton (~410Ma),

135   the Kilkieran Pluton (~400Ma), then later intrusions at ~380Ma *e.g.*, Costelloe

136   Murvey granite (**Feely *et al.,* 2010) – see Figure 1**. Finally, mid-Palaeozoic

137   composite dolerite-rhyolite diking represents the last magmatic episode **(Mohr, 2004;**

138   **Mohr *et al.,* 2018**). **Feely *et al.,* (2010**) have shown that the temporal assembly of the

139   GGC reflects episodic and long-lived granite emplacement (~40Ma) in tandem with

140   granite-related Mo-mineralization.

141   The GGC hosts numerous fluorite veins that contain a combination of the following

142   minerals: chalcopyrite, galena, pyrite, quartz, calcite, barite and chlorite – see

143   **O'Raghallaigh *et al.* (1997)** for a spatial distribution map together with descriptions

144   of the fluorite veins. More recently Moreton and Lawson (2019) described fluorite

145   and associated minerals from the Lettermuckoo quarry in the GGC. **O'Connor *et al.,***

146   **(1993**) reported that vein fluorite not only postdates the GGC, but also cuts a dolerite

147   dike in the Costelloe Murvey granite quarry **(Figure 1)**. The results of fluid inclusion

148   studies of the vein fluorite, fluorite rare earth element (REE) abundances modelling

149   and ^{40}Ar-^{39}Ar geochronometry of the dolerite dike by **O'Connor *et al.,* (1993)**

150   concluded that the dolerite dike emplacement and the transecting fluorite

151   mineralisation occurred in mid-Triassic times triggered by continental rifting of the

152   Atlantic margin in western Ireland. However, subsequent studies by **Jenkin *et al.,***

153   **1997; Menuge *et al.,* 1997; O'Reilly *et al.,* 1997; and Jenkin *et al.,* 1998** proposed

154   that the mid-Triassic age determined by **O'Connor *et al.,* (1993)** for the dike reflects

155   the timing of the hydrothermal fluorite mineralisation only. Recently, **Mohr *et al.,***

156   **(2018)** re-investigated the age of the dolerite dike populations in south Connemara

157   and noted that the pervasive hydrothermal alteration of the mid-Palaeozoic (late

158   Devonian) dolerite dikes in the GGC, including that from **O'Connor *et al.,* (1993)**, is

159   linked to the hydrothermal fluorite mineralization.

160

161   **The geological setting of the samples from Larkin's Connemara Granite Quarry.**

162   Larkin's Connemara Granite Quarry (53°20'19''N; 9°26'29''W) in Shannapheasteen,

163   south Connemara, covers an area of ~ 200m x 170m and is ~50m east of the R372

164   (**Figure 2**). It is located within the area mapped by **Leake (2006)** as the

165   Shannapheasteen Finegrained (0.5-1.5mm) Granite (SFG) which is very poorly

166   exposed. This SFG intrudes the Kilkieran pluton by block stoping **(Leake, 2006).**

167   Larkin's quarry is located on an stoped block of the Kilkieran Pluton's foliated

168   Porphyritic Granite whose main exposure occurs c.250 m to the west. The quarry has

169   been in operation for ~10 years and the foliated quarry granite is used for road

170   construction and hard landscaping in the region. The quarry granite type is light grey,

171   coarse grained (0.5–1.5cm) and inequigranular and porphyritic with approximately 30

172   vol.% quartz, 40 vol.% plagioclase, 20 vol.% K-feldspar and 10 vol.% biotite. It has a

173   well developed vertical-dipping biotite fabric (**Figure 3a**). The granite, technically a

174   granodiorite (**Streckeisen, 1967**), is cut by: *1)* a ~10 cm wide molybdenite bearing

175   quartz vein (**Figure 3b**). The vein is exposed along strike for c.2m and the

176   molybdenite mainly occurs along the vein wall, *2)* a c. 50cm wide quartz porphyry

177   dike (**Figure 3c**) can be mapped discontinuously along strike for ~100m. It is cut by

178   the fluorite vein and and the dolerite dike. The latter offsets the porphyry, in a sinistral

179   sense by ~20m. Centimetric scale fluorite veins transect the porphry close to the main

180   fluorite vein. *3)* the NW trending, ~1.5m wide, vertical dolerite dike (**Figure 3d**)

181   extends the length of the quarry and is deeply weathered. Millimetric scale fluorite

182   veinlets also cut the dolerite. *4)* A NW trending ~5m wide fluorite vein (**Figure 3e**)

183   that extends beyond the quarry's boundary. The descriptive 'fluorite vein' does not

184   adequately describe this mineralised structure. It is a fluorite-bearing granodiorite

185   breccia. The breccia is composed of angular and sub-rounded blocks of the host

186   granodiorite that range up to 0.5 metre in their longest dimension. The granite blocks

187   have not been significantly rotated. It is similar to a crackle breccia which is defined

188   as a type of breccia where the clasts have been separated by planes of rupture but have

189   experience little or no displacement (Shukla and Sharma, 2018). Vugs, containing

190   exceptional gem quality fluorite crystals, occur between the granite blocks. This type

191   of structure is similar to the Green Ridge Breccia in the Snoqualmie Granite of the

192   Cascades (**Feely *et al.,* 2017**) where gem quality amethyst bearing vugs cement

193   brecciated host granite blocks. The gem fluorite occurs as cubes, octahedra,

194   dodecahedra and in combinations of these crystal forms. The colours of the fluorite

195   range from clear to deep purple and green hues. Crystallographically controlled colour

196   zoning displaying deep purple and relatively clear zones are common especially in the

197   combination forms (**Costanzo and Feely, 2019**; **Figure 4**).

198   In summary, field relationships indicate that the quartz porphyry dike and the Mo-

199   bearing quartz vein are related to the granodiorite. The fluorite mineralisation is the

200   youngest event because the dolerite dike, and indeed the granodiorite related quartz

201   porphyry dike, are cut by millimetric to centimetric scale veins of fluorite.

202   Three samples were taken for geochronology and fluid inclusion studies (see below).

203   An additional Mo bearing quartz vein sample, GBM, from the Costelloe area (**Figure

204   1**) is included in this study. Sample GBM is from a NE striking vertical 2 cm thick

205   quartz vein that along its wall contains abundant molybdenite and chalcopyrite both of

206   <3mm grain size. The quartz vein can be traced along strike for 5 m and cross-cuts a

207   coarse grained (5–10 mm) granodiorite in the Kilkieran pluton. A molybdenite Re-Os

208   age of ~383Ma (youngest age yet determined for molybdenite in the GGC) has

209 already been published by **Feely *et al.* (2010)** from this vein and we use this

210 opportunity to present new fluid inclusion microthermometry from the vein quartz.

211

212 **Sampling and Analytical Methods**

213 Three samples were taken for geochronology and fluid inclusion studies *i.e.* LQ-1: the

214 quarry granodiorite (U-Pb zircon chronometry); LQ-2: the Mo-bearing quartz vein

215 (Re-Os chronometry and vein quartz fluid inclusion microthermometry), LQ-3: vein

216 fluorite for fluid inclusion microthermometry and GBM from the Costelloe area (fluid

217 inclusion microthermometry of vein quartz).

218 *Zircon U-Pb Geochronology*

219 A 5kg sample of the quarry granodiorite (LQ-1) was analyzed for U-Pb Chemical

220 Abrasion Isotope Dilution Thermal Ionization Mass Spectrometry (CA-ID-TIMS)

221 zircon geochronology. The sample was prepared at the University of North Carolina

222 (UNC), Chapel Hill, USA, by crushing using a jaw crusher and a disc mill. Zircons

223 were isolated using standard density (water table and heavy liquids) and magnetic

224 separation techniques. Individual zircon grains were selected using a binocular

225 microscope to represent the size and morphology range present in the samples.

226 Selected zircon grains were thermally annealed for 48 hours at 900°C and then

227 chemically abraded for 4 hours at 220°C in order to eliminate volumes affected by

228 radiation damage and to remove inclusions (**Mundil *et al*., 2004; Mattinson, 2005**).

229 Abrading the zircons for additional time caused complete dissolution of the grains,

230 due to their metamict characteristics. All zircon analyses were of single crystals.

231 Zircons were spiked using a ^{205}Pb-^{233}U-^{236}U tracer (**Parrish and Krogh, 1987**) and

232 dissolved following a procedure modified after **Krogh (1973)** and **Parrish (1987)**. U

233 and Pb were isolated using HCl anion exchange chromatography procedures modified

234   after **Krogh (1973)**. Isotope ratios of both U and Pb were determined by thermal

235   ionization mass spectrometry (TIMS) on an Isotopx Phoenix mass spectrometer at

236   UNC, Chapel Hill. Uranium was run as an oxide after loading in silica gel on single

237   Re filaments. Lead was loaded in silica gel on single zone-refined Re filaments. Both

238   U and Pb were analyzed in single-collector peak-switching mode using a Daly ion-

239   counting system. In-run U fractionations were calculated based on the measured value

240   for $^{233}U/^{236}U$ in the spike, and Pb fractionation was estimated to be 0.15%/amu based

241   on replicate analyses of NBS 981. Data processing and age calculations were

242   completed using the applications Tripoli and U-Pb Redux (**Bowring *et al.*, 2011;**

243   **McLean *et al.*, 2011**). Decay constants used were $^{238}\lambda=1.55125E^{-10}$ and $^{235}\lambda=9.8485E^{-10}$

244   ^{10} (**Jaffey *et al.*, 1971**).

245   *Molybdenite Re-Os Geochronology*

246   A 2 kg sample of vein quartz (LQ-2), that hosts fine-grained (2-4 mm) disseminations

247   of molybdenite, was sent to Durham University for molybdenite Re–Os

248   geochronometry in the Laboratory for Source Rock and Sulfide Geochemistry and

249   Geochronology and the Arthur Holmes Laboratory. Detailed sample preparation and

250   analytical protocols are given by **Selby and Creaser (2001); Selby and Creaser**

251   **(2004); Selby *et al.*, (2007); Lawley and Selby (2012)**. In brief, molybdenite was

252   isolated from the quartz vein using traditional mineral separation techniques

253   (crushing, Frantz magnetic separation, heavy liquids [MI and LST], and water

254   floatation). Additional purification (removal of remaining silicates) was achieved

255   using a room temperature HF dissolution (**Lawley and Selby, 2012**). An aliquant

256   (~30mg) of the molybdenite separate was digested in a 3:1 mix of $HNO_3:HCl$ (inverse

257   *aqua regia*) with an known amount of mixed isotope tracer (^{185}Re and normal Os) in a

258   carius tube at 220ºC for 24 hrs. Osmium was purified from the acid mix using solvent

259 extraction ($CHCl_3$) and micro-distillation methods. Rhenium was purified using

260 NaOH-acetone solvent extraction and anion chromatography (Li *et al*., 2017). The

261 purified Os and Re were loaded to Pt and Ni filaments, respectively. The isotope

262 ratios were measured using Negative Thermal Ionization Mass Spectrometry on a

263 Thermo Scientific TRITON mass spectrometer using Faraday collectors. Although

264 insignificant compared to the Re and ^{187}Os abundance in the molybdenite sample, all

265 data was blank corrected (Re = 2 picograms (pg); Os = 0.1 pg, with an $^{187}Os/^{188}Os$

266 blank composition of 0.17 ± 0.02, n = 1). The Re-Os uncertainties are reported at the

267 2σ absolute level, which were determined through error propagation of uncertainties

268 related to Re and Os mass spectrometer measurements, tracer calibration, sample and

269 tracer solution weight, reproducibility of Re and Os standards, as well as uncertainties

270 related to the blank determination. Results of analyses of the Henderson molybdenite

271 reference material (RM8599 - 27.695 ± 0.038 Ma) reported by **Li *et al.* (2017**)

272 overlap with the analysis of this study. A ^{187}Re decay constant of $1.666\times10^{-11}\,y^{-1}$ with

273 an uncertainty of 0.31% was used in the calculation of the Re-Os dates (**Smoliar *et***

274 ***al*., 1996; Selby *et al*., 2007**).

275 *Fluid inclusion studies*

276 Transmitted polarised light microscopy was used to establish a fluid inclusion

277 classification scheme. Microthermometric analyses of suitable fluid inclusions hosted

278 by the molybdenite bearing vein quartz (LQ-2 and GBM) and vein fluorite (LQ-3)

279 were then carried out at the Geofluids Research Laboratory, National University of

280 Ireland, Galway, Ireland. Doubly polished fluid inclusion wafers of each of the

281 samples (~100μm thick) were studied using a Linkam THMGS 600 heating-freezing

282 stage, mounted on an Olympus transmitted light microscope. The instrument was

283 calibrated according to the method outlined by **MacDonald and Spooner (1981)**

284   using synthetic fluid inclusion standards (pure CO_2 and water). Precision is $\pm$ 0.2°C

285   at -56.5°C and $\pm$ 0.5°C at 300°C. The microscope is equipped with a range of special

286   extra-long working distance objective lenses ranging up to x100 magnification.

287

288   **Results**

289   *Zircon U-Pb Geochronology*

290   Individual zircons separated for this study were fairly metamict, commonly hosted

291   inclusions and ranged from 90 to 210 µm along the elongate axis prior to chemical

292   abrasion. All zircon U-Pb ages reported in this study are concordant within analytical

293   and decay constant uncertainties (**Figure 5; Table 1**). T_H-corrected $^{206}Pb/^{238}U$ zircon

294   age determinations are used for all interpretations because this chronometer provides

295   the most precise and accurate estimate for rocks of this age (e.g., Schoene, 2014).

296   Individual zircon grains from the quarry granodiorite (LQ-1) yield $^{206}Pb/^{238}U$ ages

297   ranging from 407.28 to 401.06 Ma, with six grains overlapping within uncertainty at

298   401.89 Ma and three older grains (407.28, 406.56 and 405.76 Ma).

299

300   *Molybdenite Re-Os Geochronology*

301   The molybdenite sample LQ-5-2 possesses ca. 161 ppm Re and 680 ppb ^{187}Os (**Table**

302   **2**). The ^{187}Re and ^{187}Os molybdenite data yield a Re-Os model date of 401.0 $\pm$

303   0.2/1.6/2.0 Ma (uncertainties presented as analytical /+ tracer /+ decay constant

304   uncertainties; **Table 2**).

305

306   *Fluid inclusion microthermometry*

307 Four principal types of fluid inclusions (*i.e.* Type 1, 2, 3 and 4) have been observed

308 based upon the number of phases (liquid [L]; vapour [V]; solid [S]) present at room

309 temperature (~20°C) (**Table 3**).

310

311 **Type 1** inclusions are two phase (L+V; L>V) aqueous inclusions and they are

312 recorded in all samples. The degree of fill, F (F = vol. of liquid/ [vol. of liquid +

313 vapour]) of Type 1 inclusions is ~0.7–0.9. The inclusions occur either as isolated

314 individuals, in clusters or in trails. Their size ranges from 2 to 20μm in their longest

315 dimension (fluorite hosted FIs range up to ~200 microns) and display a range of

316 morphologies, varying from negative crystal shape to rounded morphologies. Type 1

317 are the dominant petrographic type in the molybdenite vein quartz samples LQ-2 and

318 GBM and in the vein fluorite sample LQ-3.

319 **Type 2** are monophase (L) aqueous inclusions and display rounded to negative crystal

320 shape morphologies and range from 2 to 20μm (vein fluorite Type 2 range up to 100

321 microns) in their longest dimension. They occur as clusters of individuals or as trails

322 in all samples.

323 **Type 3** are multi-phase (L + V + S) aqueous inclusions. They are generally rounded

324 in shape and range from 5 to 20μm (but can range up to 200μm) in their longest

325 dimension. They are only observed in the fluorite where they occur in trails and

326 clusters.

327 **Type 4** are two phase (L+ S) aqueous inclusions. They display rounded to negative

328 crystal shape morphologies and range from 5 to 100μm in longest dimension. They

329 occur in clusters or trails and are only observed in the vein fluorite.

330 Type 1 two-phase aqueous primary (using the petrographic criteria of **Roedder, 1984**)

331 fluid inclusions were chosen for microthermometry **(Figure 6)** and isochore based

332 pressure-temperature modeling. On freezing of the Type 1 inclusions to -110°C and

333 subsequent heating the temperature of eutectic melting, the temperature of hydrohalite

334 melting (T_{Mhyd}), the temperature of last ice melting (T_{LM}) and the temperature of liquid

335 to vapour homogenization (temperature of homogenization T_H) were measured. Type

336 1 inclusions hosted by the vein fluorite commonly showed eutectic melting of ~ -52°C

337 indicating the presence of $CaCl_2$ in addition to NaCl. The "crazy paving" texture that

338 reflects first melting at the H_2O-NaCl-$CaCl_2$ ternary minimum (**Shepherd *et al.*, 1985**)

339 was observed in many of the fluorite hosted primary Type 1 inclusions. Last

340 hydrohalite (NaCl.2H_2O) melting temperatures and last ice melting temperatures

341 (T_{LM}) were obtained by the method of sequential heating (**Shepherd *et al.*, 1985**). The

342 microthermometric data was then used to calculate fluid compositions in the system

343 $CaCl_2$-NaCl-H_2O (**Steele-MacInnis, *et al.*, 2011**). Furthermore, Type 1 fluid

344 inclusions that displayed eutectic melting at ~-25°C to ~ -20°C indicate general fluid

345 compositions varying from NaCl+KCl+H_2O to NaCl+H_2O. T_{LM} values were used to

346 calculate salinities (eq. wt.% NaCl), using the equations of **Bodnar (1993)**. On heating

347 of the inclusions, the temperature of homogenization (T_H), always to the liquid phase,

348 was recorded. In general, the T_H represents the minimum temperature of fluid

349 trapping. **Table 4** presents a summary of the microthermometric data obtained for the

350 Type 1 primary fluid inclusions in the three samples. Bivariate plots of T_H and salinity

351 (eq. wt.% NaCl) for the Type 1 fluid inclusions trapped in the two molybdenite vein

352 quartz samples (LQ-2 and GBM) and vein fluorite (LQ-3) are presented in **Figure 7**.

353 **Figure 7** also displays, for comparative purposes, the fields defined by the three main

354 fluid types recorded in the GGC by **Feely and Hogelsberger (1991), Gallagher *et al.***

355 **(1992) O'Reilly *et al.* (1997) and Jenkin *et al.* (1997).** The Type 1 FIs trapped in the

356 molybdenite vein quartz samples display a similar range of T_H values (~180-280°C),

357   however, GBM FIs display a broader range of salinities i.e. ~4.0–10.0 eq. wt. % NaCl

358   compared to LQ-2 (~0.4–5.0 eq. wt.% NaCl). The microthermometric data for the

359   Type 1 FIs in both Mo-bearing quartz veins plot outside and below the field defined

360   by the late magmatic aqueous-carbonic fluids associated elsewhere in the GGC with

361   the Mo-mineralization. Indeed they plot in the field defined by **O'Reilly *et al.* (1997)**

362   as representing magmatic heat-driven convection of meteoric fluids mixing with late

363   magmatic fluids into the granite.

364   Type 1 fluid inclusions hosted by the vein fluorite have significantly higher salinities

365   (~10–25 eq. wt.% NaCl) and lower T_H values (~100–200°C). These are broadly

366   similar to those values recorded from the vein fluorite that cuts the Costelloe Murvey

367   granite (CMG) and the dolerite dike in the CMG quarry (**O'Connor *et al.,* 1993**). The

368   variation in salinity and T_H displayed by these fluorite hosted Type 1 fluid inclusions

369   overlap with the field that according to **O'Reilly *et al.* (1997)** and **Jenkin *et al.* (1997)**

370   reflect the mixing of a high T meteoric fluids with a lower T and high salinity basinal

371   brine (**Figure 7**). **O'Reilly *et al.* (1997)** and **Jenkin *et al.* (1997)** argued, using fluid

372   inclusion and stable isotope data that the hydrothermal fluids responsible for

373   deposition of the fluorite veins in the GGC (like the LQ-3) involved the mixing of two

374   main fluid types. These were a meteoric, high-T (~205°C) and moderate salinity (~12

375   eq. wt% NaCl) fluid probably of late-Triassic age mixing with a lower T (~125°C)

376   high salinity (>21 eq. wt% NaCl) fluid interpreted as a basinal brine from Lower

377   Carboniferous sediments. The calculated $CaCl_2$-NaCl-H_2O compositions of Type 1

378   inclusions hosted by the vein fluorite from Larkin's quarry, and for comparison, from

379   the CMG quarry, are shown in **Figure 8**. In general, there is an overlap in fluid

380   composition ranges from the two fluorite vein localities. Furthermore, the fluid

381   compositions from these two locations plot in the composition field of granite quartz

382   hosted fluids interpreted by **Conliffe and Feely, (2010**) as reflecting incursions of

383   Carboniferous and/or Triassic fluids into onshore Irish granite basement.

384

385   **Discussion**

386   *Interpretation of Zircon Geochronology Data*

387   The zircon U-Pb data presented in this study span a range beyond the uncertainty of

388   individual analyses. This is a common feature of modern CA-ID-TIMS U-Pb zircon

389   datasets, as technical developments have permitted the reduction of uncertainties on

390   individual analyses (*e.g.* **Samperton *et al*., 2015; Widmann *et al*., 2019**). There are

391   several models to interpret an age from such chronology data: (1) zircon antecrysts

392   are abundant in igneous rocks, and therefore, only the youngest grain reflects

393   crystallization at the emplacement level (*e.g.*, **Schaltegger *et al*., 2009**); (2) protracted

394   magma crystallization is recorded by the entirety of the zircon spectrum, therefore the

395   entire age range reflects the age of the rock (*e.g.*, v**on Quadt *et al*., 2011; Wotzlaw *et**

396   ***al*., 2013**); and (3) samples can contain both antecrystic grains and grains suffering

397   from Pb-loss (*e.g.*, **Ovtcharova *et al*., 2015**). The zircon age spectra for the sample of

398   this study is best categorized as two distinct populations, at approximately ~406.5 and

399   402 Ma, with no overlap. Therefore it is most likely that either the older population

400   reflects antecrystic grains or the younger population has undergone Pb-loss and is

401   artificially young. As it is highly unlikely that Pb-loss would affect multiple grains

402   with precisely the same isotopic offset towards a young age, we interpret that the

403   older apparent ages to reflect the presence of antecrysts. Antecrystic zircon are not

404   uncommon amongst porphyritic intrusions, and have been identified in multiple other

405   CA-ID-TIMS studies of intrusions associated with mineralization (*e.g.*, **Chelle-**

406   **Michou *et al*., 2014; Buret *et al*., 2017; Gaynor *et al*., 2019**).

407   The remaining six, younger grains overlap and are normally distributed around a

408   mean value, however calculating a weighted mean age with all six grains yields a

409   MSWD of 4.0. While all of the grains overlap within uncertainty of the mean of

410   401.89 ± 0.33Ma, the high MSWD value suggests these grains may not represent a

411   single population. As such, we suggest there are two possible ways to interpret this

412   age distribution: (1) that subtle amounts of antecrystic inclusions within the age

413   spectra bias the age towards an older age (2) that the two youngest reflect subtle

414   amounts of Pb-loss, artificially generating a younger age. The first interpretation

415   yields a weighted mean age of 401.08 ± 0.54 Ma (MSWD =0.01), and the second

416   yields a weighted mean age of 402.39 ± 0.42 Ma (MSWD = 1.8). Both of these

417   situations to cause similar age spectra from other igneous zircons associated with

418   alteration (*e.g.*, **Chelle-Michou *et al.*, 2014; Ovtcharova *et al*., 2015; Buret *et al*.,**

419   **2017; Gaynor *et al*., 2019**). There are no aspects of this dataset which could indicate

420   one specific interpretation to be more geologically accurate, and both interpretations

421   overlap with the weighted mean age calculated using all grains. Therefore we instead

422   accept the weighted mean and uncertainty of all ~402 Ma as the preferred age for the

423   quarry granodiorite sample LQ-1, 401.89 ± 0.33Ma, as a more inclusive interpretation

424   of a complicated zircon age spectra.

425

426   *Re-Os molybdenite age*.

427   Including uncertainties, the new Re–Os molybdenite age (401.0 ± 0.2/1.6/2.0 Ma) for

428   the LQ-5-2 Mo bearing quartz vein from Larkin's quarry is in excellent agreement

429   with the U-Pb zircon age (401.89 ± 0.33 Ma) for the host granodiorite LQ-1.

430   *Fluid inclusion microthermometry*

431   The high-T, moderate salinity aqueous carbonic fluids associated with Mo-

432   mineralization (Feely and Hogelsberger, 1991, **Gallagher *et al*., 1992, O'Reilly *et al.,***

433   **1997** and **Feely *et al.,* 2007**) were not encountered in the Mo-bearing LQ-2 and GBM

434   quartz veins. The Type 1 moderate-T and low-moderate salinity (1–10 eq. wt.%

435   NaCl) FIs recorded in the two veins (LQ-2 and GBM) are directly comparable to the

436   two-phase aqueous inclusions of low to moderate salinity recorded throughout the

437   GGC (Feely and Hogelsberger, 1991; **Gallagher *et al*., 1992; O'Reilly *et al.,* 1997**

438   and **Feely *et al.,* 2007**). The apparent absence of aqueous-carbonic fluids in the LQ-2

439   and GBM samples is in keeping with **O'Reilly *et al*. (1997**) who noted the rare

440   occurrence of carbonic-rich fluid inclusions east of the Shannawona Fault (SF) in the

441   GGC. The exposed deeper levels of the GGC east of the SF (**Leake, 2006**) may

442   account for the scarcity of CO_2-bearing fluids, since they will tend to concentrate at

443   higher levels within a batholith. However, the evidence here suggests that the

444   presence of aqueous – carbonic fluids is not essential for molybdenite mineralisation.

445   The lower T, $CaCl_2$-bearing aqueous fluids of moderate-high salinity (10-25 eq. wt.%

446   NaCl) encountered in the vein fluorite samples (LQ-3 and COS-2 and COS-4) are

447   similar to the late Triassic fluids described by **O'Reilly *et al*. (1997) and Jenkin *et***

448   ***al.,* (1997**).

449   *The Molybdenite mineralization*

450   The molybdenite Re–Os and zircon U-Pb chronometry shows that the Mo-

451   mineralization (LQ-2) is essentially contemporaneous with the crystallization of the

452   host quarry granodiorite (LQ-1) at   401 Ma. Therefore, the timing of Type 1 fluid

453   entrapment in LQ-2 is also   401 Ma. Furthermore, the Type 1 fluids in the GMB

454   quartz vein were trapped at ~380 Ma, the age of the molybdenite mineralization

455   (**Feely *et al.,* 2010**). The computer program FLUIDS (**Bakker, 2003**) was used to

456 generate isochores in P-T space for the Type 1 aqueous fluids in both samples (**Figure**

457 **9**). **Feely *et al.*, (2007)** determined a molybdenite Re-Os age of ~423 Ma for

458 molybdenite bearing quartz veins in the Omey pluton and presented a P-T model for

459 Mo mineralization using fluid inclusion microthermometry and aureole pressure

460 constraints of 2.50 ± 0.25 kbar from **Ferguson & Al-Ameen (1985)** - see **Figure 9**.

461 Previously, **Gallagher *et al.* (1992)** used fluid inclusion microthermometry and stable

462 isotope data to generate a P-T model for Mo mineralization (Re-Os molydenite age

463   410 Ma, **Selby *et al.*, 2004**) in the Carna pluton, which yielded pressures of 1.2-2.0

464 kbar and a temperature range of 360–450°C (**Figure 9**). A higher pressure and lower

465 temperature regime prevailed during Mo-mineralization, in the Omey pluton which

466 was followed by a lower pressure and higher temperature regime during Mo-

467 mineralisation in the younger Carna pluton (see **Figure 9**). The isochores for LQ-2

468 (Re-Os age ~401 Ma) and GMB (Re-Os age ~383 Ma) plot to the left of the Carna

469 pluton's P-T field suggesting isobaric (assuming a P regime similar to the Carna

470 pluton field) shifts to lower T conditions with increasingly younger phases of

471 plutonism and accompanying Mo-mineralization.

472 *The hydrothermal fluorite mineralization*

473 Isochores for fluorite veins that postdate dolerite diking in the GGC are presented in

474 **Figure 9**. The samples are a) vein fluorite sample LQ-3, b) vein fluorite sample COS-

475 2, that cuts the dolerite dike in the CMG quarry and c) vein fluorite sample COS-4,

476 that cuts the CMG in the same quarry. The latter two isochores are redrawn using

477 microthermometric data for COS-2 and COS-4 in **O'Connor *et al.* (1993).** The

478 dolerite dikes are members of the mid-Palaeozoic (Late Devonian?) dike suite (**Mohr**

479 ***et al.*, 2018**) that transect the GGC. **O'Connor *et al.* (1993)** reported a Triassic

480 $^{40}Ar/^{39}Ar$ age (~233Ma) for this dolerite dyke which is cut by the fluorite vein COS-2.

481 However, this age for dike emplacement was reinterpreted as reflecting late-Triassic

482 hydrothermal mineralisation which was responsible for fluorite veining and

483 perturbation of the dolerite chronometers *e.g.* ^{40}Ar/^{39}Ar (**Jenkin *et al.,* 1997, 1998,**

484 **Menuge *et al.*, 1997 and Mohr *et al.*, 2018**). The isochores plot to the left of the

485 GGC P-T field in **Figure 9** and are constrained by an assumed lithostatic pressure of

486 ~1kbar equivalent to a sedimentary cover over the GGC, of ~3.5km proposed by

487 **O'Connor *et al*. (1993)** and is in keeping with the late-Triassic pressure constraint of

488 ~0.7kbar proposed by **Jenkin *et al.* (1997).**

489

490 **Summary and conclusions**

491 The field relationships exposed in Larkin's quarry encapsulates a geological history of

492 granite emplacement (Kilkieran pluton) at ~400 Ma, penecontemporaneous

493 molybdenite mineralisation and porphyry dike emplacement. The dolerite dike was

494 likely emplaced during late Devonian times (305 Ma?). During the late Triassic, vein

495 fluorite±galena±chalcopyrite±sphalerite±calcite±quartz±barite) mineralization

496 occurred forming in this instance a crackle breccia, maybe due to lithostatic pressure

497 being less than hydrothermal fluid pressure during tectonic activity (**Shukla and**

498 **Sharma, 2018**). The angular centimetric scale granite blocks are cemented together

499 by vuggy gem quality hydrothermal fluorite. Fluorite veining also occurs in the

500 deeply weathered dolerite dike and the granite related porphyry dike. Fluid inclusion

501 studies show that the Mo mineralisation (LQ-2 and GBM) was depositied during

502 mixing of late magmatic and meteoric fluids of moderate T (~250°C) and moderate–

503 low salinity (<10 eq.wt.% NaCl). Fluorite (LQ-3) hosted fluid inclusions yield

504 microthermometric data in keeping with evidence of fluid mixing between basinal

505 brines and meteoric waters.

506   A P-T-t model **(Figure 9)** tracing the spatial and temporal development of late

507   magmatic and hydrothermal mineralisation in the GGC shows that Mo mineralisation

508   occurred in tandem with the plutonic assembly of the GGC. Combined fluid inclusion

509   data, and U-Pb and Re-Os geochronometry have shown that prolonged granite-related

510   molybdenite mineralization in the GGC was initiated in the NW by the emplacement

511   of the Omey Granite at ~423 Ma, and then to the SE by the Carna (at ~410 Ma) and

512   Kilkieran (at ~400 Ma) plutons and finally by the 380 Ma Costelloe Murvey granite

513   (**Feely *et al.,* 2007; 2010**). Furthermore, the P-T model in **Figure 9** plots a change

514   with time in P-T conditions from the NW to the SE as the GGC assembled over a

515   period of ~40 million years.

516   In the North Atlantic onshore regions, granite related molybdenite mineralization is

517   documented throughout the UK, Irish and Newfoundland Caledonian-Appalachian

518   Orogen (**Lynch *et al.,* 2009; Feely *et al.*, 2010; Holdsworth *et al.,* 2015**). The broad

519   timing (and fluid characteristics) of the Mo mineralization in the UK sector *e.g.* Loch

520   Shin and Grudie Granite veins (c. 428 Ma; **Holdsworth *et al.,* 2015**) is similar to that

521   of the Ballachulish and Kilmelford igneous complexes, including the Lagalochan

522   porphyry Cu–Mo system (c. 433Ma–426 Ma; **Conliffe *et al.,* 2010**), and predates that

523   of the Etive Igneous Complex (c. 415 Ma; **Porter and Selby, 2010**), and Shap granite

524   (c. 405 Ma; **Selby *et al.*, 2008**). Mo mineralization in the Ackley granite

525   (Newfoundland sector) occurred ~380Ma (**Lynch *et al*., 2009**). Granite-related Mo

526   mineralization in the GGC of the Irish sector of the Caledonian–Appalachian Orogen

527   spanned ~40Ma from ~ 425 – 380 Ma and overlaps with the range of ages above

528   (**Feely *et al.,* 2010**).

529   **Jenkin *et al.* (1997)** argued that the hydrothermal fluorite veins in the GGC represent

530   late-Triassic mineralisation and forms part of a broader North Atlantic-European

531 Triassic-Jurassic hydrothermal mineralisation province identified by **Mitchell and**

532 **Halliday (1976)**. This model involved the rifting of the N Atlantic triggering crustal

533 thinning and subsidence of continental crust and initiating hydrothermal activity at the

534 margins of Mesozoic basins thus facilitating hydrothermal vein fluorite mineralisation

535 in for example, granite basement rocks like the GGC (**Mitchell and Halliday, 1976;**

536 **Halliday and Mitchell 1984; O'Connor *et al.,* 1993**).

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855

856 **Figure Captions**

857

858 **Figure 1.** Geological map of the Galway Granite Complex (GGC) showing the spatial

859 disribution of major lithologies and structures (adapted from **Feely _et al_., 2006 and**

860 **Leake 2006**). The early plutons are: Roundstone granite (R), Inish granite (I), Omey

861 granite (O), Letterfrack (L). D is the Delaney Dome Fm. comprising lower

862 Ordovician metavolcanic rocks. Quarry Locations 1: Larkin's Quarry

863 Shannpheasteen; 2: Costelloe Murvey Granite Quarry. Location of sample GBM is

864 also shown.

865

866 **Figure 2.** A composite map of Larkin's Quarry derived using a combination of aerial

867 photography and mapped geological features. Samples used in this study are: quarry

868 granodiorite (LQ-1), molybdenite-bearing quartz vein (LQ-2) and the main fluorite

869 vein (LQ-3).

870

871 **Figure 3.** A selection of field photographs from Larkin's Quarry. a) Quarry

872 granodiorite showing vertical-dipping biotite fabric. b) The molybdenite-bearing

873 quartz vein. c) Feldspar porphyry dike cut by millimetric scale veinlets of fluorite. d)

874 Deeply weathered dolerite dyke exposed at south-eastern end of the quarry. e) The

875 main fluorite vein with insets highlighting the brecciated nature of the host quarry

876 granodiorite (bottom left) and the exceptional quality of the fluorite crystals in the

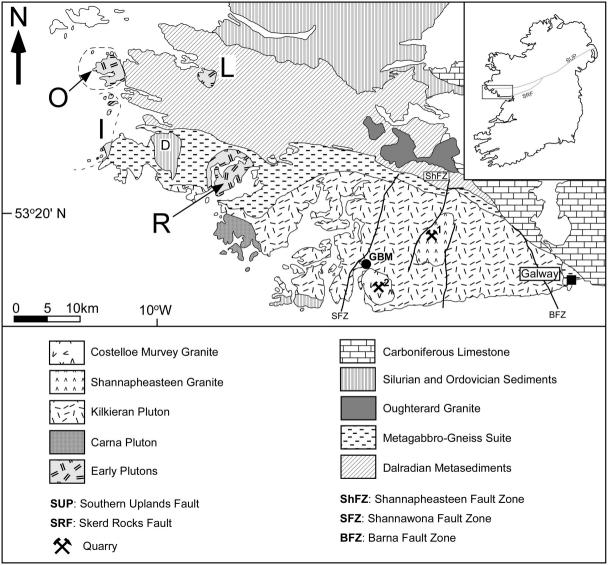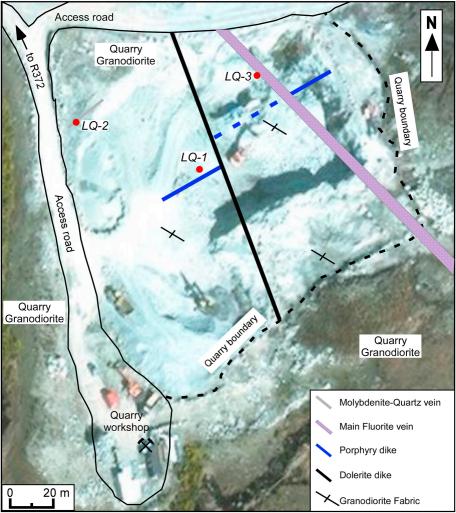877 anastomosing fluorite vugs (top right).

878

879   **Figure 4.** Gem fluorite crystals from Larkin's Quarry. The bicolour crystal (~2cm in

880   width, centre of the image) is a cube and octahedron combination. Purple-coloured

881   octahedral faces contrast with the colourless transparent cubic faces.

882

883   **Figure 5.** a) U-Pb concordia plot of zircons analysed from the quarry granodiorite

884   sample (LQ-1) and b) Weighted mean plot of U-Pb zircon ages for LQ-1.

885

886   **Figure 6.** A selection of photomicrographs showing primary two-phase

887   (liquid+vapour; L>V) fluid inclusions hosted by a) molybdenite-bearing vein quartz

888   (GBM), b) molybdenite-bearing vein quartz (LQ-2) and c) vein fluorite (LQ-3).

889   Homogenisation temperatures (T_H) and salinities (eq.wt.%NaCl) for some of the FIs

890   are also shown.

891

892   **Figure 7.** Bivariate plots of temperature of homogenisation (T_H) and salinity (eq.

893   wt.% NaCl) showing fields of the three main fluid types after **O'Reilly *et al*., (1997)**.

894   The aqueous-carbonic fluids are associated with molybdenite mineralization. The

895   lower-T aqueous fluids of low to moderate salinity formed from mixing between late

896   magmatic and meteoric fluids. The third group represents late Triassic hydrothermal

897   fluids with higher salinity and lower temperature. The data from this study are plotted

898   to show the similarities between the aqueous fluids hosted by the molybdenite-bearing

899   vein quartz (LQ-2 and GBM) and the vein fluorite (LQ-3).

900

901   **Figure 8.** A comparative plot of modelled fluid inclusion compositions from vein

902   fluorite in the Costelloe Murvey Granite quarry (COS-2 and COS-4; n=19)

903   (O'Connor *et al.,* 1993) and from the Larkin's Granodiorite Quarry at

904   Shannapheasteen (LQ-3; n=32). The grey field is based upon fluid compositions

905   recorded by Conliffe and Feely, 2010 from Irish granite basement.

906

907   **Figure 9**: Pressure-temperature space showing isochores for primary Type 1 FIs from

908   molybdenite-bearing vein quartz (LQ-2 and GBM) and fluorite veins (LQ-3, COS-2

909   and COS-4). Isochores LQ-2 and GBM are constrained by pressure estimates from

910   Gallagher *et al.* (1992). Shaded P–T fields for Mo-mineralization in the Omey pluton

911   (Feely *et al.,* 2007) and the Carna pluton (Gallagher *et al.*, 1992) are also shown. The

912   ages shown are Re-Os ages for magmatic molybdenite mineralization in the GGC.

913   The vein fluorite isochores LQ-3, COS-2 and COS-4 are constrained by an assumed

914   lithostatic pressure of 1 kbar equivalent to a sedimentary cover of ~3.5km. The

915   parameters used for the construction of the isochores are shown on the top corner of

916   the P-T space diagram.

917

918   **Table 1.** U-Pb Zircon data for mineralized granite

919

920   **Table 2.** Re-Os molybdenite data from sample LQ-2.

921

922   **Table 3:** Fluid inclusion types observed in the molybdenite-bearing vein quartz

923   samples (LQ-2 and GBM) and in the vein fluorite sample (LQ-3). Qualitative

924   assessment of fluid inclusion abundance is: X - low to medium abundance; XX - high

925   abundance.

926

927   **Table 4:** Microthermometric data for primary Type 1 inclusions in the two

928   molybdenite-bearing vein quartz (GBM and LQ-2) and vein fluorite (LQ-3). T_{FM}:

929 temperature of first ice melting; T_{Mhyd}: temperature of hydrohalite melting; T_{LM}:

930 temperature of last ice melting; T_H: temperature of homogenization; eq. wt.%:

931 equivalent weight per cent; (-) = not observed. The salinity (NaCl +$CaCl_2$) was

932 calculated using the model of Steele-MacInnis, *et al.,* 2011.

Costelloe Murvey Granite

Shannapheasteen Granite

Kilkieran Pluton

Carna Pluton

Early Plutons

SUP: Southern Uplands Fault
SRF: Skerd Rocks Fault

⚒ Quarry

Carboniferous Limestone

Silurian and Ordovician Sediments

Oughterard Granite

Metagabbro-Gneiss Suite

Dalradian Metasediments

ShFZ: Shannapheasteen Fault Zone
SFZ: Shannawona Fault Zone
BFZ: Barna Fault Zone

Access road

Quarry
Granodiorite

to R372

Access road

Quarry
Granodiorite

LQ-2

LQ-3

LQ-1

N

Quarry boundary

Quarry
Granodiorite

Quarry boundary

Quarry
Granodiorite

Quarry
workshop

0   20 m

	Molybdenite-Quartz vein
	Main Fluorite vein
	Porphyry dike
	Dolerite dike
	Granodiorite Fabric

a

Th-corrected

LQ-1

Zircon
weighted mean 206Pb/238U (Th-corrected)
401.89 ± 0.33/2.8/2.8
MSWD = 4.0, n = 6

$^{206}Pb/^{238}U$

$^{207}Pb/^{235}U$

b

Zircon
weighted mean 206Pb/238U (Th-corrected)
401.89 ± 0.33/2.8/2.8
MSWD = 4.0, n = 6

a

$T_H = 218.9°C$
Salinity = 3.9 eq. wt.% NaCl

$T_H = 213.1°C$
Salinity = 3.2 eq. wt.% NaCl

$T_H = 249.86°C$
Salinity = 3.7 eq. wt.% NaCl

20 µm

b

$T_H = 216.6°C$
Salinity = 5 eq. wt.% NaCl

$T_H = 206°C$
Salinity = 1.7 eq. wt.% NaCl

$T_H = 204.6°C$
Salinity = 1.1 eq. wt.% NaCl

20 µm

c

$T_H = 146.6°C$
Salinity = 24.1 eq. wt.% NaCl

$T_H = 145.8°C$
Salinity = 24.1 eq. wt.% NaCl

$T_H = 143.5°C$
Salinity = 24 eq. wt.% NaCl

25 µm

H$_2$O
(100 wt.%)

CaCl$_2$
(30 wt.%)

NaCl
(30 wt.%)

+ LQ-3
○ COS-2
● COS-4

Molybdenite
mineralization
(magmatic)

| | LQ-2 | T_H:225°C salinity: 1 eq.wt.%NaCl |
| | GBM | T_H:240°C salinity: 5 eq.wt.%NaCl |

Fluorite
mineralization
(hydrothermal)

	LQ-3	T_H:161°C salinity: 19.6 eq.wt.%NaCl
	COS-2	T_H:124.4°C salinity: 17.4 eq.wt.%NaCl
	COS-4	T_H:176°C salinity: 18 eq.wt.%NaCl

*Molybdenite
magmatic
mineralization
(~423-383Ma)*

Omey Pluton
~423 Ma

Carna Pluton
~410 Ma

LQ-2 ~401 Ma
GBM ~383 Ma

*Fluorite
hydrothermal
mineralization
(~233Ma)*

COS-2   LQ-3   COS-4

ID	Conc.		Th^{b}/U	$\dfrac{^{206}\mathrm{Pb}^{c}}{^{204}\mathrm{Pb}}$	$\dfrac{^{206}\mathrm{Pb}^{d}}{^{238}\mathrm{U}}$	error (%)	$\dfrac{^{207}\mathrm{Pb}^{d}}{^{235}\mathrm{U}}$	error (%)	$\dfrac{^{207}\mathrm{Pb}^{d}}{^{206}\mathrm{Pb}}$	error (%)	ages (Ma)^{d}			corr. coeff.	total common Pb (pg)
	U (ng)	Pb^{a} (pg)									$\dfrac{^{206}\mathrm{Pb}}{^{238}\mathrm{U}}$	error (Ma)	$\dfrac{^{207}\mathrm{Pb}}{^{235}\mathrm{U}}$		
F-2	0.81	51.86	0.295	3649.94	0.065083	0.17	0.492731	0.41	0.05491	0.29	406.556	0.660	406.770	0.801	0.92
F-4	0.47	31.13	0.417	688.72	0.065203	0.20	0.495904	1.45	0.05516	1.33	407.283	0.799	408.926	0.605	2.90
F-5	0.55	37.42	0.535	609.54	0.064441	0.19	0.489411	1.66	0.05508	1.55	402.664	0.757	404.509	0.639	3.83
F-6	0.63	42.61	0.520	1349.83	0.064467	0.19	0.487842	0.80	0.05488	0.70	402.823	0.740	403.439	0.600	1.94
F-8	0.73	50.05	0.574	1768.67	0.064952	0.17	0.491973	0.64	0.05493	0.54	405.756	0.656	406.254	0.662	1.71
F-10	0.24	16.47	0.511	362.94	0.064334	0.27	0.487357	2.83	0.05494	2.65	402.019	1.067	403.108	0.669	2.91
F-13	0.32	21.25	0.444	1053.53	0.064175	0.19	0.487391	1.00	0.05508	0.90	401.058	0.726	403.131	0.570	1.27
F-17	0.26	17.45	0.472	415.61	0.064257	0.24	0.487035	2.40	0.05497	2.25	401.553	0.944	402.888	0.647	2.70
F-18	0.33	21.76	0.461	1012.58	0.064184	0.21	0.487487	1.06	0.05508	0.96	401.112	0.798	403.197	0.555	1.35

[a] radiogenic Pb.

[b] Th contents calculated from radiogenic ^{208}Pb and the ^{207}Pb/^{206}Pb date of the sample, assuming concordance between U-Th and Pb systems.

[c] measured ratio corrected for fractionation only. All Pb isotope ratios were measured using the Daly detector, and are corrected for mass fractionation using 0.15 %/amu.

[d] corrected for fractionation, spike, blank and Th disequilibrium. All common Pb is assumed to be blank.

All errors except error in the ^{206}Pb/^{238}U age are reported in percent at the 2σ confidence interval. Error in the ^{206}Pb/^{238}U age is reported in absolute (Ma) at the 2σ confidence interval.

TYPES	Type 1	Type 2	Type 3	Type 4
PHASES PRESENT	L+V	L	L+V+S	L+S
FILL	0.7-0.9	-	0.5-0.9	-
SHAPE	rounded to negative crystal shape	rounded to negative crystal shape	rounded to negative crystal shape	rounded to negative crystal shape
SIZE (μm)	<2 to 200	<2 to 100	5 to 200	5 to 100
DISTRIBUTION	Clusters and isolated	clusters and trails	clusters and isolated	clusters and trails
GRANITE QUARTZ	XXX	XX	X	-
MOLYBDENITE VEIN QUARTZ	XXX	XX	-	-
VEIN FLUORITE	XXX	XX	XX	XXX

Sample	T_{FM} (°C)	T_{Mhyd} (°C)	T_{LM} (°C)	T_H (°C)	Eq. wt.% NaCl	Eq. wt.% $CaCl_2$
Molybdenite Vein Quartz (GMB)	-26.5 to -19.8 (Av. -23.4) *n=5*	-	-7.1 to -1.1 (Av. -3.3) *n=16*	176 to 284.3 (Av. 232) *n=16*	1.9 to 10.6 (Av. 5.3) *n=16*	-
Molybdenite Vein Quartz (LQ-2)	-28 to -20 (Av. -26) *n=12*	-	-3 to -0.2 (Av. -0.5) *n=22*	187.6 to 281.5 (Av. 223.8) *n=22*	0.4 to 5 (Av. 0.8) *n=22*	
Vein Fluorite (LQ-3)	-57 to -48.2 (Av. -54.3) *n=35*	-25.3 to -22.1 (Av. -23.8) *n=32*	-23.5 to -5.9 (Av. -17.0) *n=35*	90.6 to 214.0 (Av. 160.8) *n=35*	9.1 to 24.6 (Av. 19.6) n=35	1.6 to 8.8 (Av. 6.2) *n=32*

Sample	wt(g)	Re (ppm)	±	187Re (ppm)	±	187Os (ppb)	±	Age	±^	±*	±#
RO1047-1_LQ-5-2	0.030	161.28	0.55	101.37	0.35	679.52	1.91	401.0	0.2	1.6	2.0

^uncertainty including only mass spectrometry uncertainty

*uncertainty including all sources of analytical uncertainty

#uncertainty including all sources of analytical uncertainty plus decay constant

A review of molybdenite, and fluorite mineralization in Caledonian granite basement, western Ireland, incorporating new field and fluid inclusion studies, and Re-Os and U-Pb geochronology.

Martin Feely[1]*, Alessandra Costanzo[1], Sean P. Gaynor[2,3], David Selby[4] and Emma McNulty[1]

[1] Geofluids Research Group, Earth and Ocean Sciences, School of Natural Sciences, National University of Ireland Galway, Galway, Ireland
[2] Department, of Geological Sciences, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina, 27510, USA
[3] *Now at* Department of Earth Sciences, University of Geneva, rue des Maraîchers 13, Geneva, Switzerland
[4] Department of Earth Sciences, Durham University, Durham, UK

Highlights

- New discovery of late-Triassic gem quality fluorite in Connemara, Ireland.

- Late-magmatic quartz vein-hosted molybdenite in the Caledonian Galway Granite.

- 40My period of molybdenite mineralization.

- New geochronometry (Re-Os, U-Pb) and fluid inclusion studies from the GGC.