1	THE ORIGIN OF SPODUMENE PEGMATITES ASSOCIATED WITH THE LEINSTER
2	GRANITE IN SOUTHEAST IRELAND
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12	Abstract
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14	Rare-element pegmatites have diverse chemical signatures and are important sources of strategic
15	metals such as Li, Cs and Ta. The two main hypotheses to explain rare-element pegmatite formation
16	are 1) residual magmas from granitic rocks' crystallization, and 2) partial melts from a relatively rare-
17	element-rich source. In southeast Ireland, spodumene and spodumene-free pegmatite dykes occur
18	along the eastern margin of the S-type Leinster Granite batholith. With indistinguishable emplacement
19	ages around 400 Ma, the origin of the Li-rich pegmatitic fluids has been suggested to have resulted
20	from extreme fractional crystallization of Leinster Granite granodiorite magma. To test this
21	hypothesis, we used whole-rock geochemistry of pegmatite and granodiorite samples from drill cores
22	and geochemical modeling of <i>in situ</i> crystallization and batch melting to investigate which process
23	better explains the formation of pegmatites. Chemical signatures for pegmatites and granodiorite do
24	not indicate a direct comagmatic relationship, as granodiorite has higher concentrations of many
25	incompatible elements than the pegmatites (e.g. concentrations of Zr, Ti and Y). Concentrations of Li,
26	Rb, Cs, Sr and Ba show no clear fractionation trends from granodiorite to pegmatite. The in situ
27	crystallization model using the average granodiorite composition as initial magma generates a range
28	of compositions that does not include pegmatites, so it is unlikely that they represent residual granitic
29	magmas. Modeling of partial melting indicates that Leinster Granite granodiorite and pegmatite
30	magmas could have been formed in separate events and from chemically different source rocks, with
31	pegmatite magmas presumably formed in a younger event because pegmatites intrude granodiorite.
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33	Keywords
34	Spodumene pegmatite; Leinster Granite; geochemical modeling; in situ crystallization; batch melting;
35	petrogenesis.
36	
37	INTRODUCTION

39 Rare-element pegmatites display very diverse chemical signatures and are enriched in elements that are usually present in low concentrations in other rocks. These features make them important 40 41 sources of a wide range of commodities, including industrial minerals, gemstones and strategic 42 metals. Two alternative petrogenetic processes have been proposed to explain the formation of rare-43 element pegmatites: 1) extensive fractionation of fertile parental granitic magma, with rare-element 44 pegmatites representing the residual phase in this process; or 2) partial melting of rare-element-rich 45 source rocks. Pegmatites geographically associated with granitic batholiths have often led to support 46 for the first hypothesis that granitic rocks and pegmatite magmas have a comagmatic relationship. 47 Several studies have successfully demonstrated the link between parent granite and pegmatites, 48 including examples in Canada (Černý et al. 2012) and Spain (Roda-Robles et al. 2012). However age 49 and/or geochemical incompatibilities, such as pegmatites being significantly older than granite, or an 50 apparent absence of parental granite, are often documented (e.g. Walker et al. 1989, Muller et al. 51 2015).

52 One way to approach and resolve the petrogenetic problem is to use quantitative trace element 53 modeling and mathematically test different models. We use this approach for a pegmatite belt in 54 southeast Ireland, which is associated with the peraluminous Leinster Granite. A genetic link between 55 them has been suggested based on age and geochemical similarities (O'Connor et al. 1991, Whitworth 56 & Rankin 1989), but the exact relationship between them remains uncertain. As a result of new 57 lithium exploration drilling being carried by Blackstairs Lithium Ltd., an extensive lithogeochemical 58 database is available that provides drill core of the entire thickness of several pegmatite dykes. 59 Coupled with textural and mineralogical observations on the drill core, these are used for geochemical 60 modeling to better constrain the origin of these rare metal pegmatites.

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# 62 GEOLOGICAL SETTING AND PREVIOUS STUDIES

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The geology of the southeast of Ireland is dominated by Paleozoic basement and igneous intrusions (Fig. 1). The basement is composed of sedimentary and associated volcanic rocks regionally metamorphosed to lower greenschist facies and is subdivided into the following units and lithologies: greywacke and shale of the Cambrian Bray and Cahore Groups; mudstone, siltstone and sandstone of the Ordovician Ribband Group; deep marine shale, now commonly slate, with abundant intermediate to acidic volcanic rocks of the Ordovician Duncannon Group; and the deep marine turbidite sequence of the Silurian Leinster Inlier (Graham & Stillman 2009, Holland 2009).

The largest of the younger igneous intrusions is the Leinster Granite, a Caledonian batholith composed at least in part of sheeted intrusions (Grogan & Reavy 2002) of S-type two-mica granitic rocks (predominantly granodiorite) intruded into the metasedimentary basement. The batholith is part of the Trans-Suture Suite (Brown *et al.* 2008), which spans the trace of the Iapetus suture in Britain 75 and Ireland. According to the same authors, the origin of these granitic magmas is related to orogen-76 wide sinistral transfersion during the early Devonian, triggering lamprophyre magma generated by 77 melting of Avalonian lithospheric mantle to rise and transfer heat to the lower part of the Avalonian 78 crust, forming partial melts with S-type granitic composition. The Leinster Granite comprises five 79 plutons aligned with the NE-SW regional strike of the Lower Paleozoic supracrustal country rocks 80 (McConnell & Philcox 1994). Despite its size, the batholith is poorly exposed. Most available data are 81 from the better exposed Northern pluton, including a U-Pb monazite age of  $405 \pm 2$  Ma (O'Connor *et* 82 al. 1989). It has been assumed that all plutons intruded and crystallized simultaneously (Brindley 83 1973) and therefore that this age applies to the whole batholith. However a wide variability in initial 84 Sr and Nd isotope ratios, both between and within plutons, has been interpreted as resulting from the 85 generation of different magma batches by partial melting of an isotopically heterogeneous 86 sedimentary source (Mohr 1991). In addition, disequilibrium textures in plagioclase phenocrysts 87 indicate a multi-stage and multi-scale acid-acid mixing of magma batches during ascent and 88 emplacement (Grogan & Reavy 2002).

89 A network of lithium pegmatite dykes, metres to tens of metres thick, is known from at least nine 90 localities along the eastern margin of the Tullow Lowlands pluton and within the schist septum that 91 separates it from the Blackstairs Unit to the south (Fig. 1). There are almost no outcrops of these 92 dykes and the localities have been identified by concentrations of glacial boulders, in several cases 93 confirmed by mineral exploration drilling (Steiger & von Knorring 1974, Steiger 1977). Most of the 94 dykes so far detected roughly follow the NE-SW regional structure of the Caledonian East Carlow 95 Deformation Zone (McArdle & Kennedy 1985). They intrude the Tullow pluton, minor granitic 96 bodies related to the Leinster Granite and guartz-mica schist formed by contact metamorphism of the 97 Leinster Granite with the Ribband Group. Rb-Sr isotope studies of the pegmatites (O'Connor et al. 98 1991) yielded a whole-rock errorchron age of  $396 \pm 7$  Ma (MSWD = 5.54), constructed using 99 spodumene pegmatites, associated lepidolite greisens and barren pegmatites. This corresponds to an age of  $402 \pm 7$  Ma when recalculated using the recent IUGS recommendation on <sup>87</sup>Rb half life (Villa 100 101 et al. 2015). The pegmatite errorchron initial Sr ratio of  $0.705 \pm 0.005$  (O'Connor et al. 1991) lies 102 within the Leinster Granite range obtained by Mohr (1991). Moreover, results from fluid inclusion 103 analysis (Whitworth & Rankin 1989) and mineral chemistry (Whitworth 1992) suggest a genetic link 104 between the Leinster Granite and lithium pegmatites. Despite the indistinguishable Caledonian ages of 105 granitic rocks and pegmatites and their similar initial Sr isotope ratios, it is debatable whether lithium 106 pegmatites represent the residual magma after crystallization of the Leinster Granite, or were formed 107 from separate partial melts of similar or different metasedimentary sources. Here we aim to better 108 constrain the petrogenesis of the pegmatite belt and its relationship with the Leinster Granite.





Fig 1: Spodumene pegmatite occurrences in southeast Ireland. Dykes are restricted to the eastern
margin of the Tullow Lowlands pluton, spatially associated with the East Carlow Deformation Zone
(ECDZ). Pegmatites intrude both the Tullow pluton and metasedimentary rocks of the Ribband
Group.

# 115 CHARACTERIZING THE LEINSTER RARE-ELEMENT PEGMATITE BELT AND COUNTRY ROCKS

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A recent mineral exploration drilling programme has provided an opportunity to study the Leinster
spodumene pegmatites, barren (spodumene-free) pegmatites and their immediate country rocks. The
rock types identified in the drill cores in the study areas of Aclare and Moylisha (Fig. 1) are:

(1) Spodumene pegmatite: coarse-grained (crystals up to 10 cm), composed of spodumene (1040%), albite (25-35%), quartz (15-20%), Li-muscovite (10-15%), spessartine (5%) and minor K-

122 feldspar, apatite, cassiterite and sphalerite (all less than 5%). Spodumene, albite and Li-muscovite are 123 present as well-formed subhedral crystals, while quartz is interstitial. The dykes can be unzoned, or 124 present zoning when thicker than 10 meters, with an increase in modal spodumene towards the quartz 125 and feldspar core (Fig. 2). In some dykes, crystals of spodumene are aligned perpendicular, and 126 sometimes parallel, to the dyke margins. These observations suggest that each pegmatite dyke has 127 formed by the progressive *in situ* crystallization of a single body of magma. Fine grained albite-rich 128 (85-90%) aplitic patches are common within all zones and include around 10% combined quartz and 129 muscovite, with accessory apatite, cassiterite, spessartine, beryl and Mn,Fe-phosphate.

(2) Barren (spodumene-free) pegmatite: coarse-grained (typically 4 cm, maximum 10 cm),
consisting of K-feldspar (10-20%), albite (20-30%), quartz (20-35%), muscovite (15-20%) and
spessartine (2-5%). K-feldspar and albite occur as subhedral prismatic crystals, with later quartz and
muscovite. Quartz-feldspar intergrowth (graphic texture) is common.

(3) Granodiorite (Leinster Granite): medium-grained granodiorite consisting of quartz (30-45%),
oligoclase (30-40%), microcline (10-20%), biotite (5-10%) and muscovite (2-5%), locally porphyritic
with occasional 2 cm plagioclase phenocrysts. Sparse tourmaline is observed in some of the contact
zones with spodumene pegmatite and its veinlets.

(4) Quartz-mica schist (Ribband Group): fine- to medium-grained schist consisting of biotite (4050%), muscovite (20-30%), quartz (20-25%) and minor arsenopyrite, titanite and apatite, with a
foliation defined by mica; late tourmaline porphyroblasts with poikiloblastic texture are present up to
20 cm from the contact with spodumene pegmatite.

Spodumene pegmatite dykes crosscut both granodiorite and quartz-mica schist in Aclare, and granodiorite only in Moylisha. The contacts between spodumene pegmatite and Leinster Granite are defined by irregular planes and narrow (up to 10 cm) zones of interaction between the two rock types. Contacts between spodumene pegmatite and mica schist are sharp and parallel to the foliation in the mica schist. Spodumene-free pegmatites occur only within granodiorite, against which their contacts are diffuse.





Fig. 2: Mineral and chemical profiles of zoned spodumene pegmatite (drill core ACL13-04). Modal
spodumene (open rectangles) increases towards the quartz-feldspar core. Albite-rich aplite occurs as
patches throughout the dyke. Whole-rock chemical compositions measured for homogeneous intervals
of rock correlate with the mineralogical variation.

- 153
- 154 METHODS
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## 156 Sampling and geochemical analysis

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158 Eight mineral exploration drill cores with close to 100% recovery from two localities, Aclare (6 159 cm diameter) and Moylisha (4 cm diameter), were split in half and divided into homogeneous rock 160 parts, between 7 cm and 3.05 m long, resulting in 281 samples. These parts were then crushed, 161 decomposed using a four acid digestion and analysed for 48 elements by ICP-MS by ALS Minerals 162 (Loughrea, Co. Galway, Ireland). Routine practices were used to ensure data quality control: sample 163 duplicates (1 in every 20 samples), homogeneous quartz pebbles (1/40) and certified standards (1/20). 164 Results showed reproducibility between duplicates within 15% for most elements, except Ta, Zr and 165 Ce, and no contamination problems. Detection limits for the elements analyzed range between 0.002 166 and 100 ppm. Whole-rock geochemical analysis of pegmatites can be problematic because of their 167 large crystal size, demanding large volume samples for representative results. However, the 168 pegmatites sampled from drill core in the present study have a typical grain size of around 2 cm, with

the largest, rare, crystals having grain sizes less than 10 cm, which facilitates representative whole-rock sampling.

171 Pegmatite drill cores were subdivided for whole-rock analysis by lithology into aplite, spodumene-172 rich pegmatite, pegmatite without spodumene, granodiorite and quartz-mica schist. Weighted mean 173 compositions of each rock type were then calculated for each drill core. For example, in a drill core in 174 which granodiorite constituted a total length of 4.8 m, three samples of lengths 1.6 m, 1.2 m and 2.0 m 175 were analysed. Mean concentrations were then calculated by weighting analyses proportional to the 176 rock volumes in these three core lengths. In the case of pegmatite dykes, the calculation comprised all 177 the intervals from the upper to the lower contact with the country rocks. Contact zones with visible 178 and/or chemical haloes in country rocks and granitic lenses within pegmatites were excluded from the 179 estimated bulk compositions. The method assumes that the drill core samples are representative of the 180 pegmatite bodies as a whole and therefore does not allow for possible chemical variation along strike 181 or down dip within the dykes. It is also assumed that each pegmatite dyke crystallized from a single 182 batch of magma and that bulk pegmatite concentrations of the key elements remained constant during 183 and after crystallization. To highlight possible heterogeneities within rock types between localitites, 184 whole-rock data is presented as the weighted mean of each rock type per drill core, for Aclare and 185 Moylisha separately.

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#### 7 Modeling of pegmatite origin by in situ crystallization of granitic magma

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189 Calculated bulk concentrations of key elements were used to test whether the Leinster pegmatites 190 could have been derived as a residual phase of continuous crystallization of Leinster Granite 191 granodiorite magma. The elements Ba, Sr, Li, Rb and Cs were chosen as petrogenetic tracers, the first 192 two as compatible elements in granitic minerals and the others as incompatible in granodioritic 193 magma but enriched in pegmatites. To estimate the mean concentrations of these key elements for the 194 Tullow Lowlands pluton, the overall mean of all granitic intervals in all drill cores was considered, 195 weighted by volume as core diameters are different for drill core from Aclare and Moylisha. The same 196 was done for pegmatites and schist, to obtain representative concentrations assuming intrusion of one 197 batch of Li-pegmatite magma and one batch of barren pegmatite magma per dyke.

198 The equation for Rayleigh fractionation has frequently been used for trace element modeling of the 199 formation of pegmatites from granitic magmas (e.g. Shearer et al. 1992, Roda-Robles et al. 2012). 200 However, the idea of crystals separating from melt through gravity is most likely only applicable to 201 ultramafic melts (Rollinson 1993). In granites and pegmatites solidification most likely starts from the 202 intrusion margins inwards and in pegmatites experimental data suggest that this is a rapid process (e.g. 203 Webber et al. 1997, 1999, London 2008, Nabelek et al. 2010). In this case, a more adequate approach 204 is the quantitative *in situ* crystallization model proposed by Langmuir (1989), in which a solidification 205 zone occurs between the crystallized margins and the central convecting magma batch in a chamber.

206 Langmuir (1989) considers the case where once solidification starts, all liquid remaining in the 207 solidification front is ultimately separated from the crystal mush and returns to the interior of the 208 magma chamber, which is a reasonable approximation of the current understanding of granite and 209 pegmatite crystallization, and from this assumption the derived equation is  $C_L/C_0 = (M_L/M_0)^{(f(D-1)/[D(1-1)/[D($ 210  $^{(f)+f]}$ , where  $C_L$  = concentration of the element in the differentiated magma;  $C_0$  = initial concentration of the element in the magma;  $M_L$  = mass of the differentiated magma;  $M_0$  = initial mass of the magma 211 212 chamber; f = fraction of magma allocated to the solidification zone which returns to the unfractionated 213 magma chamber; and D = bulk partition coefficient. The bulk partition coefficient was calculated 214 through the equation  $D = \Sigma (X_A K d_A + X_B K d_B + X_C K d_C + ...)$ , where  $X_A$  = weight fraction of mineral 215 A in the rock and  $Kd_A$  = mineral A / liquid partition coefficient. This *in situ* crystallization equation 216 also yields the result for simple Rayleigh fractionation, for the condition f = 1.

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#### 218 *Modeling of pegmatite origin by partial melting*

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220 Direct partial melting of a sedimentary source has previously been proposed as an alternative 221 mechanism to form rare element pegmatite magma (e.g. Jolliff et al. 1992, Shearer et al. 1992). The 222 most suitable process to generate the felsic melts discussed is batch melting (Shaw 1970), that can be 223 modelled by the equation  $C_L/C_0 = 1/[D_{RS} + F(1 - D_{RS})]$ , where  $C_L = \text{concentration of the element in}$ 224 the generated melt;  $C_0$  = concentration of the element in the unmelted source;  $D_{RS}$  = bulk partition 225 coefficient of the residual solid; and F = weight fraction of melt produced. The bulk partition 226 coefficient is calculated in the same way as for the in situ crystallization calculations. Minimum PT 227 conditions of partial melting can be estimated based on the minimum temperature of 700 °C to 228 produce granitic composition melts (MacRae & Nesbitt 1980) and the spodumene stability field, 229 yielding a minimum pressure around 350 MPa. Conditions considered are in agreement with the 230 thermal model for generation of S-type granitic magmas within a transtensional pull-apart zone 231 proposed by Brown et al. (2008).

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233 RESULTS

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235 Whole-rock geochemistry

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Ranges and means of whole-rock trace and major element concentrations for the four rock types and the relevant study areas are given in Table 1. The granodiorite is classified as peraluminous using the index of Shand (1943) and carries the signature of syn-collisional granites according to the trace element discrimination diagram of Pearce *et al.* (1984) (Fig. 3). Granodiorite in Aclare has lower alkali contents thus higher A/CNK and slightly lower Y and Nb contents when compared to the same rock type in Moylisha. Both types of pegmatites are also peraluminous and syn-collisional, but spodumene-free pegmatites exhibit the greater scatter in Rb, Y and Nb values. Spodumene pegmatitesin Aclare present a high scatter of A/CNK values and higher than Moylisha.

Multi-element diagrams per locality are presented on Fig. 4. Average trace element concentrations for granodiorite show relative abundances decreasing towards the more incompatible elements to the right of the plot and a strong negative Nb anomaly. Spodumene pegmatites and barren pegmatites present a multi-peak signature, with low Ba, Th, La, Ce, Sr and Zr and Y, strong negative Ti anomaly and positive Rb, Ta and Hf anomalies. In comparison with both types of pegmatites, the Leinster Granite granodiorite is enriched in the LIL elements Ba and Sr, which are compatible in feldspars, and in the light rare-earth elements La and Ce.

252 As Li is a suitable element to differentiate the three granitic rock types (granodiorite, spodumene 253 free pegmatite and spodumene pegmatite), incompatible and compatible elements were plotted against 254 this element (Fig. 5). The three rock types cluster separately without well-defined trends between 255 them. Spodumene pegmatites in Aclare have higher mean Li when compared with the same rock type 256 in Moylisha, while spodumene-free pegmatites in Moylisha present a higher mean Li concentrations 257 than those from Aclare. Granodiorite has the lowest mean Rb concentration and highest mean Sr and 258 Ba, while concentrations of Li and Cs are intermediate between spodumene-free and spodumene 259 pegmatites.

The ratio K/Rb versus Cs is controlled by K-feldspar and micas and is a useful petrogenetic index in granite-pegmatite systems (Černý *et al.* 1981) and values for the studied rock types are shown on Fig. 6. Granodiorites present the highest K/Rb ratios (50-120) and can be locally enriched in Cs as represented by one sample from Aclare. Spodumene pegmatites and barren pegmatites show lower K/Rb ratios of 20-60 and 20-90, respectively. The data do not fit on the expected evolution trend for the case of a parental granite magma fractionating to residual pegmatitic magmas. Table 1: Geochemical data for the studied rock types in the localities Aclare and Moylisha. Values in ppm. LOD = limit of detection. Duplicate analysis of 15

267 of the samples shows maximum percentage differences between the higher and lower concentration presented in the last column of the data table.

		Aclare								Moylisha						Estimatio							
	LOD (ppm)	Quar	rtz mica-sch	ist	G	ranodiorite		Spodu	mene pegm	atite	Spodum	ene-free peg	matite	G	ranodiorite		Spodu	imene pegm	atite	Spodum	ene-free peg	matite	n of repro- ducibility
		mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max	(%)
Li	0.2	236.8	97.2	445.1	395.7	188.3	569.3	7020.4	1678	10794.9	430.8	26.8	1076.5	528.4	400.3	587.7	2670.0	601.8	4144.9	204.1	151.4	221.1	8.1
Na	100	11845.9	10201.8	13752.6	29734.6	26516.7	32012.6	27310.9	18738.9	40469.7	37577.1	33686.3	57400	26201.9	25650.1	28160.2	34556.4	27540	37405.1	29523.9	28480	31939.3	4.8
K	100	24651.7	24158.2	25449.1	17492.6	15403.6	18966.7	16236.6	15481.4	17165.2	24691.2	4100	35500	29341.7	27455.5	30158.6	21950.7	16133.4	32401.4	29939.7	28562.2	30968.3	4.9
Rb	0.1	150.2	110.3	205.4	248.2	177.4	306.2	593.1	496.6	707.8	725.7	94.6	1470	281.1	245.4	314.2	559.6	364	738.9	361.0	335.4	371	8.7
Cs	0.05	26.2	6.6	61.2	125.1	30.4	277.4	77.9	63.8	99.1	77.1	15.6	418	50.6	39.4	64.7	65.5	45.6	100.8	36.4	35.8	36.8	8.2
Mg	100	11176.7	10687.1	12609.1	6669.4	5861.0	7666.7	262.0	112.3	933.9	358.4	200	400	4566.0	3962.2	4840.1	181.8	80	381.3	696.3	624.7	724.6	5.4
Ca	100	3786.0	2664.3	5370.6	14090.5	6366.7	17842.0	1787.3	969.7	6408.9	1760.6	1366.5	3200	12189.2	10457.1	12784.3	1130.6	799.9	1791.4	3436.8	3086.7	3553.9	10.2
Sr	0.2	119.8	95.1	153.7	227.0	133.9	281.1	15.3	12	29.1	16.3	9.5	40.4	158.6	137.1	171.6	16.3	11	29.9	35.3	27.6	38.5	10.0
Ba	10	499.9	482.1	520	335.0	279.2	357.3	16.7	9.7	35.9	36.4	20	50	368.2	321.0	378.3	15.3	8.4	32.9	60.6	59.3	62.3	6.9
Ti	50	4585.7	4323.3	5016.9	2094.2	2066.7	2178.6	11.1	2.9	32.6	6.0	0	100	2211.5	1914.2	2308.9	33.5	13.3	116.3	290.1	221.6	335.6	2.9
Mn	5	696.8	495.2	1190.3	500.2	416.4	590.9	935.6	741.4	1009.6	302.6	108	649	565.6	499.0	584.7	783.5	656.2	1041.1	761.7	636	902.9	8.0
Fe	100	48192.0	46395.4	50366.7	20568.5	19728.1	21000.9	4316.3	3513.3	4600	4152.4	2100	4863.1	17271.1	15905.3	17838.6	3292.2	2863.8	4007.1	5952.1	5775	6145.5	10.2
Y	0.1	15.9	14.8	18.1	6.4	5.7	7.1	0.3	0.1	1.5	0.6	0.5	0.8	8.2	7.8	8.4	0.4	0.1	2.5	4.8	3.2	6.3	13.3
Zr	0.5	105.0	97.6	115.2	37.1	34.7	40.6	12.0	9.2	15	12.2	7.6	23.2	97.5	77.2	105.3	13.4	7.8	20	21.0	19	22	15.9
Nb	0.1	13.9	13.3	14.2	6.7	5.3	7.2	28.0	24.1	33.5	33.8	11.1	109.5	8.0	7.3	8.3	34.3	22.1	45.2	10.3	9.8	11.1	7.0
Hf	0.1	3.0	2.7	3.2	1.2	1.2	1.3	1.4	1.2	1.8	1.4	1	3	2.8	2.4	3.2	2.1	1.4	2.7	1.2	1.1	1.2	8.7
Та	0.05	1.0	0.9	1.1	2.5	0.5	3.4	27.6	17.9	50.1	36.2	16.3	180	1.7	1.3	1.9	33.9	20.9	44.2	4.4	4.1	5.1	26.4
Al	100	86710.3	84007.1	89132.5	75597.8	69600.0	78509.0	68487.7	65249.5	70403	68118.4	50800	78300	74074.3	73271.9	74682.2	63341.4	53760.2	71578.5	67780.4	64332.3	71249.3	7.2
Р	10	427.5	384.3	494.9	557.6	375.8	655.3	669.0	489.1	1038.9	677.4	430	1530	864.6	751.3	922.6	503.4	386.4	745.1	537.3	461.9	659.6	5.5
La	0.5	33.9	32.7	35.9	13.9	12.1	14.9	0.2	0	1	0.3	0.1	0.7	25.7	21.6	27.9	0.2	0	0.9	3.8	2.6	4.6	8.8
Ce	0.01	73.0	71.6	74.6	28.4	23.9	29.8	0.7	0.4	2.2	1.0	0.8	1.4	57.3	48.2	60.9	0.6	0.2	2.2	8.5	6	10.4	40.1
Th	0.2	10.5	9.2	11.4	4.9	4.7	5.6	0.6	0.5	0.8	0.9	0.4	3.1	11.5	9.4	12.2	2.6	2.3	3	2.5	1.8	3	13.3

269 Values indicate minimum and maximum concentrations calculated for rock types in each drill core and the mean value is calculated as the mean of all

analysed samples from each locality weighted by volume. The volumes of core that contributed to these calculated mean concentrations are: quartz-mica

schist – Aclare and total 0.075 m<sup>3</sup>; granodiorite – Aclare 0.11 m<sup>3</sup>, Moylisha 0.13 m<sup>3</sup>, total 0.24 m<sup>3</sup>; spodumene pegmatite – Aclare 0.15 m<sup>3</sup>, Moylisha 0.05 m<sup>3</sup>,

total 0.20 m<sup>3</sup>; spodumene-free pegmatite – Aclare 0.02 m<sup>3</sup>, Moylisha 0.04 m<sup>3</sup>, total 0.06 m<sup>3</sup>.





granodiorite and pegmatites. B) Trace element discrimination diagram of Pearce et al. (1984) showing 

277 syn-collisional signature of the rock types. Data points represent mean concentrations weighted by

drill core volume of each rock type in individual drill cores.



Fig. 4: Trace element concentrations are normalized to the composition of chondritic meteorites given
by Thompson (1982). Samples in black are from Aclare and in grey from Moylisha. The diagrams are
for A) quartz-mica schist; B) granodiorite; C) spodumene pegmatites and D) spodumene-free
pegmatites. Gaps indicate no available data.



Fig. 5: Bivariate plots of Li versus A) Rb, B) Sr, C) Cs and D) Ba. Samples in black are from Aclare

and in grey from Moylisha.



Fig. 6: Cs versus K/Rb as an index of chemical evolution of pegmatites. (\*) For comparison, the
arrow indicates data presented in London (2008) for variation within a granite-pegmatite group (Red
Cross Lake, Manitoba) with a proven petrogenetic link.

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292 Partition coefficients used in modeling

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294 Modeling of both in situ crystallization and batch melting requires calculation of bulk partition 295 coefficients. As already debated in other pegmatite modeling studies (e.g. Jolliff et al. 1992, Shearer 296 et al. 1992), uncertainty of the appropriate values of bulk partition coefficients can arise for several 297 reasons. Several variables can affect mineral/melt partition coefficients, including temperature, 298 confining pressure and melt composition (Rollinson 1993), but none of these are considered to be 299 major issues in the studied granite-pegmatite systems. The partition coefficients and their published 300 sources chosen for the key elements in granitic and pegmatitic minerals are presented in Table 2. 301 Values were chosen to be representative of high-Si crystallizing magmas, consistent with the 302 predominant granodiorite in Leinster Granite, and maximum values available were used for

303 calculations in cases where the reference presented a range. Bulk partition coefficients were304 calculated considering the mineral assemblages discussed below.

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Mine ral/melt	Albite	Muscovite	Quartz & aluminosilicate	K-feldspar	Biotite
Li	0.1	1.67	0.05	0.05	1.65
reference	9	3	8	9	3
Rb	0.06	1.75	0.016	0.74	5.3
reference	6	3	7	1	1
Cs	0.44	0.24	0.044	0.13	3.1
reference	6	3	7	2	1
Sr	3.31	0.5	0.01	5	0.06
reference	4	3	assumed	5	3
Ba	0.19	5.5	0.015	6.7	7
reference	6	3	7	1	1

**306** Table 2: Crystal / melt partition coefficients used for quantitative modeling.

References: 1 Mahood & Hildreth (1983); 2 Icenhower & London (1996); 3 Icenhower & London (1995); 4 Drake & Weill (1975); 5 Long (1978); 6 Bea *et al.* (1994); 7 Nash & Crecraft (1985); 8 Jollif *et al.* (1992); 9 Walker *et al.* (1989).

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309	In situ	crystallization	modeling
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311 In situ crystallization calculations test the hypothesis that pegmatites and granodiorite are 312 genetically linked through a continuous evolution model in a closed system (Fig. 7). Whole-rock 313 concentrations of Li, Rb, Cs, Sr and Ba were estimated for granodiorite, spodumene pegmatite, barren 314 pegmatite and schist as means weighted by total drill core volume of all analyses from all drill cores, 315 for each rock type. These means for granodiorite are then considered to represent the initial magma 316 from which residual pegmatitic fluids might have evolved in the late stages of crystallization, and 317 subsequently escaped to be intruded as dykes; concentrations for schist are presented for comparison 318 only in this scenario. Fractionation paths with various combinations of parameters were calculated, to 319 show whether it is possible to reach bulk concentrations for the residual magma that are similar to 320 mean spodumene pegmatite and barren pegmatite chemical compositions. The crystallizing 321 assemblage considered is plagioclase (40%), K-feldspar (25%), quartz (25%), biotite (5%) and white 322 mica (5%).

323 In *in situ* crystallization, the enrichment of a trace element in the residual melt relative to the 324 parent melt ( $C_L/C_0$ ) varies according to the mass of residual melt relative to the total mass of the 325 magma chamber ( $M_L/M_0$ ), the fraction of liquid returned to the main magma body from the 326 solidification zone (f) and the bulk partition coefficient (D). From lithogeochemical data, the values of 327  $C_0$  were considered to be the bulk trace element concentration calculated for granodiorite as the initial 328 magma. The fraction  $M_I/M_0$  is equivalent to the fraction of residual magma and values between 0.01 329 (99% residual magma, start of crystallization) and 0.99 (1% residual magma, end of crystallization) 330 were considered. Values of f range between 0.01 (1% liquid returned from solidification zone, 331 representing very rapid crystallization) and 1 (all liquid returns from the solidification zone, 332 representing Rayleigh fractionation). The bulk partition coefficient, and therefore different values of 333 partition coefficients for the elements studied, can contribute substantially to variations in the final 334 result and this will be discussed later.

335 The ranges of possible enrichment and depletion of the five key elements, with granodiorite as 336 model initial magma, are plotted on Fig. 8. Average concentrations for key elements in pegmatites are 337 not always within the ranges of possible concentrations reached by in situ crystallization and the 338 maximum limiting Rayleigh fractionation. The magnitude of depletion in Ba and Sr and enrichment in 339 Rb and Li by *in situ* crystallization is sufficient to reach the mean composition of spodumene 340 pegmatite. However, very different crystallization conditions are required to individually explain the 341 elements analysed; for example ~95% crystallization at f ~0.8 can produce mean spodumene 342 pegmatite composition on the Ba-Li plot, whereas at least 99% crystallization is required at  $f \sim 0.3$  to 343 produce mean spodumene pegmatite on the Rb-Li plot; there are no conditions which can account for 344 the mean Cs concentration of the spodumene pegmatites. Spodumene-free pegmatite compositions are 345 even less well reproduced by in situ crystallization (Fig. 8).



Fig. 7: In situ crystallization model (Langmuir 1989) applied to the Leinster Granite granodiorite -348 349 pegmatites system, depicting continuous granodiorite-to-pegmatites evolution within the same magma 350 batch. A) Solidification starts from the margins of the magma chamber inwards, with a fraction of 351 magma returning to the main magma body. The initial magma's composition is equivalent to the bulk 352 composition of the crystallized granodiorite. B) After extensive crystallization, the residual magma 353 would have become concentrated in incompatible elements and have a composition equivalent to the 354 most evolved bulk spodumene pegmatite dykes. The same process could also generate the (less 355 evolved) spodumene-free pegmatites as an intermediate member or as another end-member.



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Fig. 8: Bivariate plots with the results of *in situ* crystallization modeling with the average Leinster Granite granodiorite as the initial magma. The arrows show the range from minimum (10%) to maximum (100%) fractions of liquid returned (f) to the main magma body from the solidification zone considered in this system – 100% returned is equivalent to Rayleigh fractionation. The grey area shows the range of values with other values of f between 0.1 and 1.

- 362
- 363 Batch melting modeling

The range of suitable initial compositions of sedimentary sources that underwent batch partial melting forming the three rock types were also calculated to assess whether a common origin for them is possible. In batch melting, the concentration of an element in the generated melt compared with the concentration of the element in the unmelted source ( $C_L/C_0$ ) varies with the weight fraction of melt

- produced (F) and the bulk partition coefficient of the residual solid in the source (D<sub>RS</sub>). The weighted 369 370 mean concentrations measured in the three rock types were considered as different values for  $C_{L}$ , 371 allowing calculation of the range of necessary concentrations in the source C<sub>0</sub> to generate melts with 372 the measured compositions. The range of initial concentrations was calculated from 1% melting (F = 373 0.01) to 99% melting (F = 0.99). In order to calculate  $D_{RS}$ , the source was estimated to be quartz 374 feldspar-rich sediment, since partial melting of pelitic sediments would result in Li, Rb and Cs being 375 retained in the mica-rich residual solid as partition coefficients are high for these elements (Jolliff et 376 al. 1992 and references therein). The residual solid considered would be mainly composed of quartz 377 (25%), feldspars (50%) and aluminosilicate (25%), thus allowing for all mica to be melted. Variations 378 in the percentages of these minerals in the residual solid and from the partition coefficients chosen do
- 379 not have major impact on the final results.

Possible initial concentrations in sources that can form melts with the compositions of average granodiorite and pegmatites are featured on Fig. 9. Considering a range of 1 to 40% of partial melting to form the three rock types (1 to 10% for pegmatites and 10 to 40% for granodiorite), the lines of initial concentrations converge to a restricted area representing little variation in the source for Rb (50 to 130 ppm), Li (30 to 430 ppm) and Cs (around 10 ppm). For Ba and Sr, initial concentrations converge to restricted areas for pegmatites (30 to 90 ppm Ba, 30 to 60 ppm Sr), but indicate a source more enriched in those elements for granodiorite (around 600 ppm Ba and 400 ppm Sr).



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Fig. 9: Bivariate plots with the results of partial melting modeling. The arrows show the possible initial concentrations of the magma source rocks for spodumene pegmatite (line 1), spodumene-free pegmatite (line 2) and granodiorite (line 3) if they underwent 1 to 99% melting. Average composition of the schist is plotted for comparison, representing metasedimentary rocks of the Ribband Group.

#### **393** IMPLICATIONS FOR SPODUMENE PEGMATITE FORMATION

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The strong negative Nb anomaly in Leinster Granite granodiorite indicates that a crustal component is involved in its formation, which can also be inferred for pegmatites, but with a less pronounced negative anomaly. Pegmatites do not always carry higher concentrations of incompatible elements than granodiorite (e.g. concentrations of Zr, Ti and Y) and no clear fractionation trends are observed among incompatible or compatible elements, or ratios that indicate chemical evolution. 400 Plotted geochemical data is scattered rather than representing a chemically closed or semi-closed 401 continuous evolution system. Although the key elements Li and Cs have not been analysed in samples 402 from elsewhere in the Leinster Granite, the chemical signature of granodiorites within the batholith 403 varies between localities, probably reflecting the multi-intrusion character of the batholith and some 404 variation in source rock composition (Mohr 1991, Sweetman 1987, Grogan & Reavy 2002).

405 With the chosen partition coefficients it is not possible to reach spodumene pegmatite mean 406 concentration considering all elements, therefore a single crystallizing system from granodiorite to 407 pegmatite. If, however, the bulk partition coefficient for Ba  $(D_{Ba})$  is double that listed in Table 2, by consequence of higher Kd<sub>Ba</sub><sup>biotite/liquid</sup> and Kd<sub>Ba</sub><sup>K-feldspar/liquid</sup>, the required depletion of this element from 408 409 granodiorite to pegmatites can be attained. Such high values were obtained experimentally by 410 Icenhower & London (1996), for example. For Rb, a slightly lower bulk partition coefficient makes 411 possible the enrichment observed in spodumene pegmatites. This would be mainly controlled by a lower Kd<sub>Rb</sub><sup>biotite/liquid</sup> and such lower values have been obtained experimentally (e.g. Icenhower & 412 London 1995). However, the spodumene pegmatite Sr and Cs concentrations cannot be reached using 413 414 reasonable partition coefficients for these elements. They could only be reached with a much higher 415 Cs bulk partition coefficient. Extreme Li concentrations found in spodumene pegmatite can be 416 reached towards high fraction of magma return from the solidification front, or Raleigh fractionation, 417 and with less than 5% magma left, but this scenario would require the combination of cumulate-type 418 crystallization followed by effective extraction of the residual magma. Therefore granodiorite-to-419 pegmatite magmatic evolution seems highly unlikely taking account of all five elements.

420 One possibility to explain the discrepancy observed when trying to correlate concentrations of key 421 elements through the Langmuir *in situ* crystallization equation is a significant loss of the mobile 422 elements Rb, Cs and Li at some stage between generation, ascent and emplacement of pegmatite 423 magma. However, very narrow exomorphic haloes (up to 20 cm) into the granodiorite and the 424 permeable quartz-mica schist do not support this hypothesis. Cs mobility does however seem possible 425 as high-Cs granodiorite is observed (Figs. 5 and 6). The mean Cs concentration for the initial magma 426 could be lower if this locally high-Cs granodiorite is considered to be part of an exomorphic halo (and 427 therefore excluded from bulk composition calculations), but still considerably higher D<sub>Cs</sub> would be 428 needed to reach pegmatite concentrations. Another possibility is contamination from country rocks, 429 especially contamination of spodumene pegmatites by the schist, but its mean composition with low 430 Li (<250 ppm), Rb (<150 ppm) and Cs (<30 ppm) cannot explain the deviations of in situ 431 crystallization trends away from pegmatite compositions.

On the other hand, with a narrow range of high source rock incompatible element concentrations and reasonable assumptions for degrees of partial melting, it is possible to form melts with the average composition of granodiorite, spodumene-free and spodumene pegmatites. However, source compatible element concentrations have to be highly variable if the three lithologies share a common source. As bulk concentrations of Ba and Sr would strongly depend on the amount of feldspars in 437 metasedimentary rocks, this variation can be explained by the presence of feldspar-rich and feldspar-438 poor source rocks, generating granodiorite and pegmatites, respectively. If pegmatite magmas were 439 generated at the same time or later than the granodioritic magmas that formed the Leinster Granite, as 440 implied by cross-cutting relationships, the required source rock heterogeneity likely existed on at least 441 a kilometre scale. Otherwise, it is difficult to envisage the pegmatite source rocks remaining unmelted 442 during Leinster Granite granodiorite magma formation.

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444 CONCLUSIONS AND FUTURE WORK

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446 Observing patterns on multi-element diagrams and bivariate plots, the behaviour of incompatible 447 elements and the absence of fractionation trends among elements, the hypothesis that pegmatite 448 magmas formed by the continuous evolution of the same magmatic system as the Leinster Granite 449 granodiorite is not a satisfactory explanation for the origin of these rocks. Specifically, in situ 450 crystallization modeling shows that it is highly unlikely that pegmatites represent the residual magma 451 from crystallization of Leinster Granite granodiorite. This requires that granodiorite and pegmatite 452 magmas were derived in separate partial melting events, the pegmatites presumably representing a 453 later event because they are observed to intrude granodiorite. However the source rocks required to 454 account for the geochemistry of pegmatites and the Leinster Granite granodiorite must be different, 455 with considerably more feldspar required in the granodiorite source rocks than in the pegmatites' 456 source rocks. An unresolved question is why magmas that formed igneous rocks in close spatial 457 association (granodiorite plutons and pegmatite dykes) were not apparently formed by partial melting 458 of the same source rocks. In an alternative scenario the voluminous Leinster Granite could represent 459 mixing between mantle-derived mafic magma and crustal melts of similar rocks that alone generated 460 pegmatite magmas. Precise dating and radiogenic isotope studies to define the sources are planned 461 towards a better understanding of the story behind the formation of pegmatites in southeast Ireland.

462

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464

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474 REFERENCES

#### 475

- BEA, F., PEREIRA, M.D. & STROH, A. (1994) Mineral/leucosome trace-element partitioning in a
  peraluminous migmatite (a laser ablation-ICP-MS study). *Chemical Geology* 117, 291-312.
- 478
- 479 BRINDLEY, J.C. (1973) The structural setting of the Leinster Granite, Ireland. Scientific Proceedings
  480 of the Royal Dublin Society A5, 27-36.
- 481
- BROWN, P.E., RYAN, P.D., SOPER, N.J. & WOODCOCK, N.H. (2008) The Newer Granite problem
  revisited: a transtensional origin for the Early Devonian Trans-Suture Suite. *Geological Magazine*145(2), 235-256.
- 485
- ČERNY, P., TRUEMAN, D.L., ZIEHLKE, D.V., GOAD, B.E. & PAUL, B.J. (1981) The Cat Lake –
  Winnipeg River and the Wekusko Lake pegmatite fields, Manitoba. *Manitoba Department of Energy and Mines, Mineral Resources Division, Economic Geology Report* ER80-1.
- 489
- ČERNY, P., TEERTSTRA, D.K., CHAPMAN, R., SELWAY, J.B., HAWTHORNE, F.C., FERREIRA, K.,
  CHACKOWSKY, L.E., WANG, X. & MEINTZER, R.E. (2012) Extreme fractionation and deformation of
  the leucogranite-pegmatite suite at Red Cross Lake, Manitoba, Canada. *The Canadian Mineralogist*50, 1839-1875.
- 494
- DRAKE, M.J. & WEILL, D.F. (1975) Partition of Sr, Ba, Ca, Y, Eu<sup>2+</sup>, Eu<sup>3+</sup>, and Other REE between
  plagioclase feldspar and magmatic liquid experimental study. *Geochimica et Cosmochimica Acta* **39**(5), 689-712.
- 498
- 499 GRAHAM, J.R. & STILLMAN, C.J. (2009) Ordovician of the south. *In:* Holland, C.H. & Sanders, I.
  500 [*eds.*] The geology of Ireland, 2<sup>nd</sup> edition, 568p.
- 501
- 502 GROGAN, S.E. & REAVY, R.J. (2002) Disequilibrium textures in the Leinster Granite Complex, SE
  503 Ireland: evidence for acid-acid magma mixing. *Mineralogical Magazine* 66(6), 929-939.
- 504
- HOLLAND, C.H. (2009) Silurian. *In:* Holland, C.H. & Sanders, I. [*eds.*] The geology of Ireland, 2<sup>nd</sup>
  edition, 568p.

- 508 ICENHOWER, J. & LONDON, D. (1995) An experimental study of element partitioning among biotite, 509 muscovite, and coexisting peraluminous silicic melt at 200 MPa (H<sub>2</sub>O). *American Mineralogist* **80**,
- 510 1229-1251.

511	
512	ICENHOWER, J. & LONDON, D. (1996) Experimental partitioning of Rb, Cs, Sr, and Ba between alkali
513	feldspar and peraluminous melt. American Mineralogist 81, 719-734.
514	
515	JOLLIFF, B.L., PAPIKE, J.J. & SHEARER, C.K. (1992) Petrogenetic relationships between pegmatite and
516	granite based on geochemistry of muscovite in pegmatite wall zones, Black Hills, South Dakota,
517	USA. Geochimica et Cosmochimica Acta 56, 1915-1939.
518	
519	LANGMUIR, C.H. (1989) Geochemical consequences of in situ crystallization. Nature 340(6230), 199-
520	205.
521	
522	LONDON, D. (2008) Pegmatites. Canadian Mineralogist, Special Publication 10, 347p.
523	
524	LONG, P.E. (1978) Experimental determination of partition coefficients for Rb, Sr, and Ba between
525	alkali feldspar and silicate liquid. Geochimica et Cosmochimica Acta 42, 833-846.
526	
527	MACRAE, N.D. & NESBITT, H.W. (1980) Partial melting of common metasedimentary rocks: a mass
528	balance approach. Contributions to Mineralogy and Petrology 75(1), 21-26.
529	
530	MAHOOD, G. & HILDRETH, W. (1983) Large partition coefficients for trace elements in high-silica
531	rhyolites. Geochimica et Cosmochimica Acta 47, 11-30.
532	
533	MCARDLE, P. & KENNEDY, M.J. (1985) The East Carlow Deformation Zone and its regional
534	implications. Geological Survey of Ireland Bulletin 3(4), 237-255.
535	
536	MCCONNELL, B.J, & PHILCOX, M.E. (1994) Geology of Kildare-Wicklow, a geological description to
537	accompany the bedrock geology 1:100,000 map series, Sheet 16, Kildare-Wicklow. Geological
538	Survey of Ireland, 70p.
539	
540	MOHR, P.J. (1991) Cryptic Sr and Nd isotopic variation across the Leinster Granite, southeast Ireland.
541	<i>Geological Magazine</i> <b>128</b> (3), 251-256.
542	
543	MULLER, A, IHLEN, P.M., SNOOK, B., LARSEN, R.B., FLEM, B., BINGEN, B. & WILLIAMSON, B.J.
544	(2015) The chemistry of quartz in granitic pegmatites of southern Norway: petrogenetic and economic
545	implications. Economic Geology 110, 1737-1757.
546	

- 547 NABELEK, P.I., WHITTINGTON, A.G. & SIRBESCU, M.C. (2010) The role of H<sub>2</sub>O in rapid emplacement
  548 and crystallization of granitic pegmatites: resolving the paradox of large crystals in highly
  549 undercooled melts. *Contributions to Mineralogy and Petrology* 160, 313-325.
- 551 NASH, W.P. & CRECRAFT, H.R. (1985) Partition coefficients for trace elements in silicic magmas.
  552 *Geochimica et Cosmochimica Acta* 49, 2309-2322.
- 553

- 554 O'CONNOR, P.J., AFTALION, M. & KENNAN, P.S. (1989) Isotopic U-Pb ages of zircon and monazite 555 from the Leinster Granite, Southeast Ireland. *Geological Magazine* **126**(6), 725-728.
- 556
- O'CONNOR, P.J., GALLAGHER, V. & KENNAN, P.S. (1991) Genesis of lithium pegmatites from the
  Leinster Granite margin, southeast Ireland: geochemical constraints. *Geological Journal* 26, 295-305.
- 560 PEARCE, J.A., HARRIS, N.B.W. & TINDLE, A.G. (1984) Trace element discrimination diagrams for the
  561 tectonic interpretation of granitic rocks. *Journal of Petrology* 25(4), 956-983.
- 562
- RODA-ROBLES, E., PESQUERA, A., GIL-CRESPO, P. & TORRES-RUIZ, J. (2012) From granite to highly
  evolved pegmatite: a case study of the Pinilla de Fermoselle granite-pegmatite system (Zamora,
  Spain). *Lithos* 153, 192-207.
- 566
- 567 ROLLINSON, H. (1993) Using geochemical data: evaluation, presentation, interpretation, 1<sup>st</sup> edition.
  568 *The Longman Geochemistry Series*, 352p.
- 569
- 570 SHAND, S. J. (1943) The Eruptive Rocks, 2<sup>nd</sup> edition. New York: John Wiley, 444 p.
- 571
- 572 SHAW, D.M. (1970) Trace element fractionation during anatexis. *Geochimica et Cosmochimica Acta*573 34, 237-243.
- 574

575 SHEARER, C.K., PAPIKE, J.J. & JOLIFF, B.L. (1992) Petrogenetic links among granites and pegmatites
576 in the harney peak rare-element granite-pegmatite system, Black Hills, South Dakota. *The Canadian*577 *Mineralogist* 30, 785-809.

- 578
- 579 STEIGER, R. (1977) Prospecting for lithium and tungsten in Ireland. *In: Prospecting in areas of glaciated terrain*, Helsinki Institution of Mining and Metallurgy, 14-24.
- 581
- 582 STEIGER, R. & VON KNORRING, O. (1974) A lithium pegmatite belt in Ireland. *Journal of Earth*583 *Sciences, Leeds Geological Association* 8, 433-443.

- 585 SWEETMAN, T.M. (1987) The geochemistry of the Blackstairs Unit of the Leinster Granite, Ireland.
  586 Journal of the Geological Society, London 144, 971-984.
- 587
- THOMPSON, R.N. (1982) Magmatism of the British Tertiary Volcanic Province. Scottish Journal of *Geology* 18, 49-107.
- 590
- 591 VILLA, I.M., DE BIÈVRE, P., HOLDEN, N.E. & RENNE, P.R. (2015) IUPAC–IUGS recommendation on
  592 the half life of <sup>87</sup>Rb. *Geochimica et Cosmochimica Acta* 164, 382–385.
- 593
- WALKER, R.J., HANSON, G.N. & PAPIKE, J.J. (1989) Trace element constraints on pegmatite genesis:
  Tin Mountain pegmatite, Black Hills, South Dakota. *Contributions to Mineralogy and Petrology* 101, 290-300.
- 597
- WEBBER, K.L., FALSTER, A.U., SIMMONS, W.B. & FOORD, E.E. (1997) The role of diffusioncontrolled oscillatory nucleation in the formation of Line Rock in pegmatite-aplite dikes. *Journal of Petrology* 38(12), 1777-1791.
- 601
- WEBBER, K.L., SIMMONS, W.B., FALSTER, A.U. & FOORD, E.E. (1999) Cooling rates and
  crystallization dynamics of shallow level pegmatite-aplite dikes, San Diego County, California. *American Mineralogist* 84, 708-717.
- 605
- 606 WHITWORTH, M.P. (1992) Petrogenetic implications of garnets associated with lithium pegmatites
  607 from SE Ireland. *Mineralogical Magazine* 56, 75-83.
- 608
- WHITWORTH, M.P. & RANKIN, A.H. (1989) Evolution of fluid phases associated with lithium
  pegmatites from SE Ireland. *Mineralogical Magazine* 53, 271-284.