

Evolution of fluid phases associated with lithium pegmatites from SE Ireland

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Abstract

Fluid inclusions in quartz from internally zoned barren and spodumene-bearing pegmatites associated with the Leinster granite of SE Ireland represent a variety of early and late hydrothermal fluids responsible for the development of pegmatites. Microthermometry and optical examination reveal two main populations of inclusions. The first (Type 1) comprises low-moderate salinity brines which homogenized at temperatures up to about 400 °C. The second (Type 2) appear to postdate the first population and are characteristically more saline and homogenized at temperatures mostly below 250 °C. Isochores for model type 1 inclusion fluids indicate that a late-magmatic/early-hydrothermal fluid developed from the Leinster granite at 675 °C and 2.5 kbar and cooled isobarically into the spodumene stability field where complete crystallization of the pegmatites took place. Later, more saline, type 2 fluids of unknown origin may have contributed to the alteration of spodumene to muscovite and albite with the accompanying release of lithium from the lattice of spodumene.

KEYWORDS: fluid inclusions, pegmatite, lithium, Leinster, Ireland, isobaric cooling.

Introduction

SPODUMENE-BEARING pegmatites in SE Ireland provide one of the main potential resources of lithium in western Europe. Since their discovery by Irish Base Metals Ltd in the early seventies, several theories for their genesis have been proposed (Scoon, 1978; Luecke, 1981; and Kennan *et al.*, 1986). The mineralogy, petrography, and major element geochemistry of the pegmatites is well documented (Steiger and von Knorring, 1974, and Scoon, 1978). However, to date, attempts at petrogenetic modelling using fluid inclusions have not been undertaken. Here we report on the results of a detailed study of the occurrence, distribution, and thermometric properties of fluid inclusion populations in quartz from two of the important spodumene-bearing pegmatite occurrences (Aclare and Monaghan, Fig. 1), their associated granites and barren pegmatites. The latter are distinguished from mineralized pegmatites by their lack of spodumene. Fluid

inclusion data reported here are used in conjunction with petrographic and mineralogical observations to establish the influence and source of the fluids associated with the development of the pegmatites.

Previous studies

The use of fluid inclusions in evaluating fluid processes in granites has been well documented by Konnerup-Madsen (1977 and 1979), Alderton and Rankin (1982), Rankin and Alderton (1983), Olsen and Griffin (1984*a* and *b*), Pêcher *et al.* (1985) and Chryssoulis and Rankin (1988). From these studies it is apparent that the quartz in granites shows a remarkable variation in terms of the nature, distribution and abundance of fluid inclusion populations. Most inclusions appear to be secondary and represent portions of late-stage post-consolidation fluids that have interacted and, on occasions, mineralized the host granite. Less commonly, fluids generated during the late-mag-

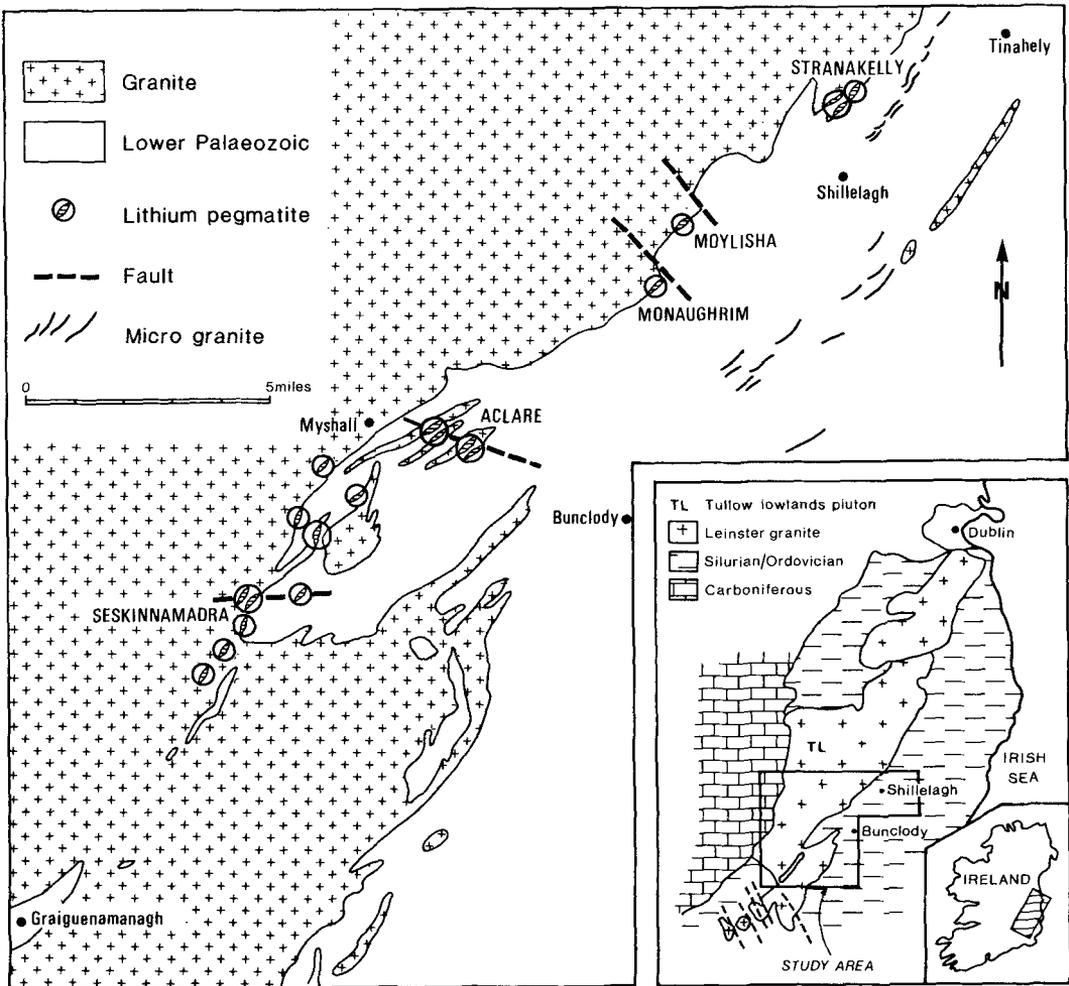


Fig. 1. Geological setting and location map of the Leinster pegmatite belt. Modified from Brindley (1973), Brück (1974), Steiger and von Knorring (1974), Brück and O'Connor (1977), and Kennan *et al.* (1986).

matic stage may be preserved as primary inclusions. However, the relationship and distinction between these various fluid generations are notoriously difficult to assess due to recrystallization of quartz and complex overprinting of later generations of inclusions on earlier inclusion populations (e.g. Rankin and Alderton, 1985; London, 1986).

Pegmatites are generally thought to represent the transition stage between late-magmatic and early-hydrothermal processes (Naumov *et al.*, 1977, and Halls, 1987). By analogy with granites, pegmatite minerals should also contain complex fluid inclusion assemblages not necessarily rep-

resentative of these late-magmatic and early-hydrothermal fluids. However, until recently very little work on fluid inclusions in granite pegmatites, particularly lithium-bearing varieties, had been reported (Weisbrod and Poty, 1975; Zakharchenko, 1971; Boyarskaya *et al.*, 1977; and Rosovskii, 1981). The most relevant work on the transition between the magmatic and hydrothermal regimes in lithium pegmatites is by London (1986) who studied inclusions in minerals from the internally zoned Li, Cs, Nb, Ta-bearing Tanco pegmatite, Bernic Lake, Manitoba. By integrating thermometric data for both aqueous and CO₂-rich inclusions in quartz, spodumene, and eucryp-

tite with the appropriate lithium aluminosilicate phase diagram, he was able to outline the P - T evolutionary path of the pegmatite.

Mineralogically and geochemically the Leinster lithium pegmatites exhibit marked similarities with those at Tanco and a similar interpretative approach, aimed at integrating fluid inclusion, petrographic and experimental data, is attempted here. However, the inclusion populations at Aclare and Monaghan are quite different to those at Tanco in that the inclusions are extremely small, poor in daughter minerals and CO_2 , and confined to quartz grains.

Geological setting

All known lithium pegmatites in the area are spatially and temporally associated with the Leinster granite of SE Ireland, the largest Caledonian batholith in the British Isles, dated at 404 ± 24 Ma (O'Connor and Brück, 1978). The batholith covers an area of approximately 1500 km^2 and is elongate in a NNE-SSW direction. Microgranite, pegmatite and aplite dykes were intruded approximately parallel to the margin of the Leinster batholith (Fig. 1.). On the basis of geochemical work, Brück and O'Connor (1977) suggested that these granite varieties were formed during the fractionation of a parent granitic melt and then further modified by hydrothermal fluids which may have also played a part in the development of the lithium pegmatites associated with the Tullow Lowlands Unit. Host rocks for the pegmatite dykes at Aclare and Monaghan are small tonalite-granodiorite intrusions (Steiger and von Knorring, 1974; Scoon, 1978) and Ordovician and Silurian greywackes, quartz arenites, siltstones, sandstones and basic to acidic volcanics (Brück *et al.*, 1979, and McArdle, 1981). Foliations in the country rocks around each pluton and within the granite are concordant with the pluton's margin (Cooper and Brück, 1983). Two other styles of mineralization are associated with the Leinster granite; base metal veins in the northern plutons (Elsdon and Kennan, 1982, and Williams and Kennan, 1983) and tungsten as scheelite in microgranites (Steiger, 1977, and Gallagher, 1987).

Spodumene was first reported in SE Ireland by Thomson (1836), and Brindley (1957) noted the presence of beryl and spodumene in pegmatite-aplite dykes in the Leinster granite. Subsequently, pegmatite boulders were identified at thirteen localities along the strike of the eastern contact of the Leinster granite (Steiger and von Knorring, 1974, and Scoon, 1978). Follow-up diamond drilling by Irish Base Metals Ltd. during the period

1970-1982 intersected five bedrock occurrences of internally zoned pegmatite dykes up to twenty metres thick containing significant developments of spodumene-rich and barren pegmatites cut by aplites. Due to the lack of field exposure, the field settings and relationships of the pegmatites are difficult to establish, but through detailed logging of available drill core it has been possible to reconstruct the internal mineralogical zoning based on generalized zones for pegmatites as defined by Cameron *et al.* (1949). Fig. 2 summarises new textural and mineralogical data on the internal structure of the pegmatite dykes at Aclare. The main minerals are quartz, spodumene (the main host of Li in the pegmatites), albite, Li-poor and Li-rich muscovite and K-feldspar with accessories such as garnet and Ta oxides (Steiger and von Knorring, 1974). Zoning is typical of many lithium-bearing pegmatites e.g. Kings Mountain, USA (Kesler, 1978; Kunasz, 1982; and London, 1988, pers. comm.) but has not been positively identified previously in Leinster. Scoon (1978) distinguished border and wall zones but ascribed a more important role to fluids replacing rock types during the development of the internal features of the pegmatite bodies.

Sampling and preparation for microthermometric analysis

Doubly polished wafers approximately 0.2 mm thick were prepared for thermometric analyses from granites and pegmatites from Aclare and Monaghan (Fig. 1). However, only the quartz contained inclusions suitable for study. This is in marked contrast to the Tanco pegmatite of Manitoba where superb inclusions, up to $150 \mu\text{m}$ long, in spodumene, have been reported (London, 1985 and 1986).

Prior to thermometric analysis, thin sections and inclusion wafers were examined petrographically in order to outline the broad characteristics of the fluid inclusion populations. Microthermometric analysis was carried out on a Linkam TH-600 stage (Shepherd *et al.*, 1985b) and calibrated using various inorganic and organic compounds of known melting points (Roedder, 1984). All temperatures reported in the range $-60 \text{ }^\circ\text{C}$ to $+25 \text{ }^\circ\text{C}$ are believed to be accurate to within $0.3 \text{ }^\circ\text{C}$, and above this temperature the maximum error is $5 \text{ }^\circ\text{C}$. The only phase transitions routinely measured were the temperature at which the last ice crystal melted (T_{lm}) and vapour-liquid homogenization temperature (T_{h}) which was always to liquid. A heating rate of $0.2 \text{ }^\circ\text{C min}^{-1}$ was used when determining T_{lm} and $5 \text{ }^\circ\text{C min}^{-1}$ when inves-

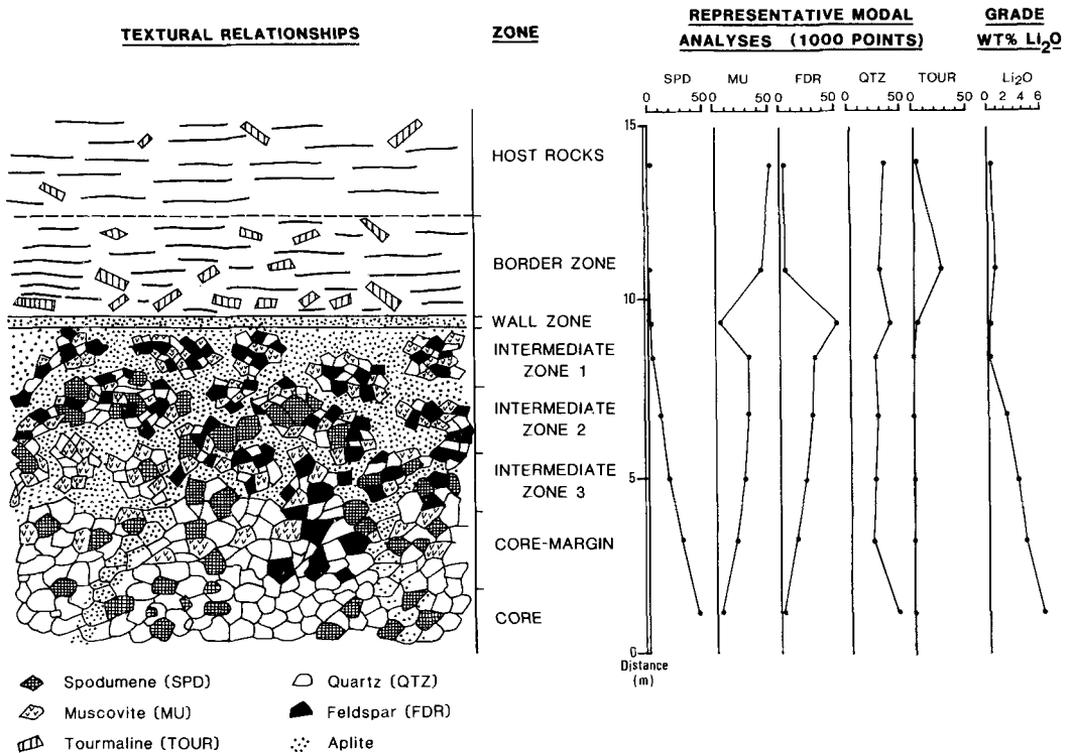


Fig. 2. Schematic cross-section through the hanging wall pegmatite at Aclare showing zoned distribution of minerals, textural relationships, and Li_2O grades. Zonal classification based on Cameron *et al.* (1949); Li_2O grades calculated visually from estimated modal analyses in drill core.

tingating T_h . The small inclusion size prevented any reliable estimates of the temperature of first melting of the ice crystals (T_{im}). Additional phase transformations, such as salt hydrate or CO_2 clathrate dissociation, were not observed. CO_2 clathrates, although suspected on cooling in a few inclusions out of the several hundred studied, could not be confirmed by crushing stage studies. Salinities modelled on the pure system $\text{NaCl-H}_2\text{O}$ were calculated from the equations presented by Potter *et al.* (1978), Hall *et al.* (1988) and the T_{im} measurements. Salinities are expressed as the equivalent weight percent NaCl. Due to the small size of inclusions available for study, problems of metastability were frequently encountered (Roedder, 1971), most notably the failure of inclusions to freeze even on cooling to -120°C and the disappearance of the vapour bubble on freezing resulting in metastable ice melting temperatures. These latter temperatures were not included in the data set because they lead to erroneous salinities (Rankin and Criddle,

1985). Inclusions showing obvious signs of necking down were not analysed.

Results

In the pegmatites, quartz varies from subhedral coarse-grained crystals attaining a maximum size of 8 cm, to heavily fractured, anhedral grains 0.5 cm in size. All contain fluid inclusions and there appears to be no systematic variation of inclusion properties with changing quartz morphology. Inclusions are mostly located in planes or clusters sometimes along recognizably healed fractures and isolated inclusions are less abundant. Crystal zoning within the quartz is absent so there is no focal point for relating various generations of inclusions. Petrographically, the occurrence of inclusions in quartz from granite appears to be identical to that in the pegmatites. Classification of the inclusion types based on origin (primary vs. secondary/pseudosecondary) is not possible so a morphological/compositional basis

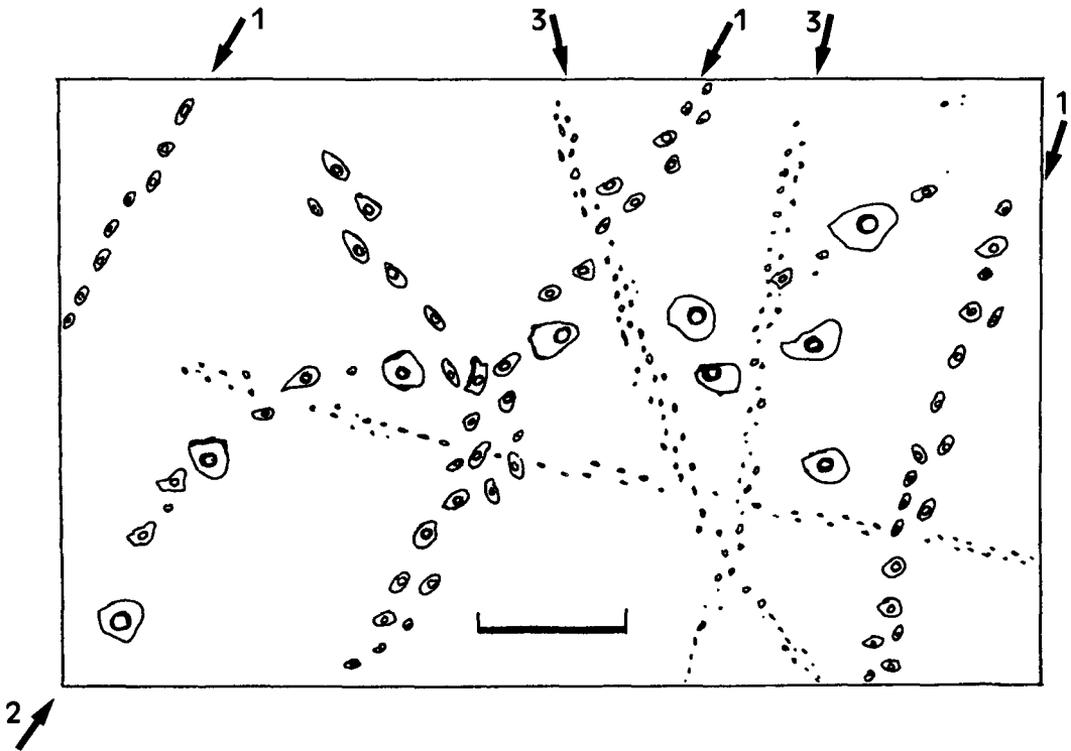


Fig. 3. Diagrammatic field of view of pegmatitic quartz showing form and distribution of inclusion types 1, 2 and 3. Scale bar = 25 μm .

for inclusion classification has been adopted in keeping with Alderton and Rankin (1982) and Rankin and Alderton (1985). In the Aclare and Monaghan granites and pegmatites three main inclusion types have been recognized, based on their morphology (Fig. 3) and thermometric properties (Fig. 4).

Type 1 are liquid-rich, aqueous inclusions up to 12 μm in size and occur in planes which are usually confined to individual quartz crystals but may cross boundaries. Ellipsoid, circular, and 'negative' crystal shapes are the most common. For all samples, type 1 inclusions homogenized over a wide temperature range; 100–400 $^{\circ}\text{C}$ with ice melting temperatures (T_{im}) between 0 and -9.0 $^{\circ}\text{C}$ corresponding to a salinity range of about 0 to 13 eq.wt. % NaCl (Fig. 4).

Type 2 are also liquid-rich, aqueous inclusions but are longer (5–18 μm) and usually more irregularly shaped. Frequently they appear to cross-cut type 1 inclusions. They show a much narrower T_{h} range mostly between 140 and 240 $^{\circ}\text{C}$ and, in marked contrast to type 1 inclusions, have a much lower

ice-melting temperature (T_{im}) range of -8 to -28 $^{\circ}\text{C}$ corresponding to much higher salinities of 11 to >23 eq.wt. % NaCl (Fig. 4). Persistence of ice and liquid below the eutectics of pure systems, NaCl–H₂O–KCl (Hall *et al.*, 1988) suggests that other ions such as Ca and/or Li (Shepherd *et al.*, 1985b) may be present in the fluids. However, we have been unable to determine the first melting temperatures in these small inclusions.

Type 3 are much less common than types 1 and 2 above, comprising on average about 10% of the total inclusion population. They are extremely small (<2 μm), monophasic, liquid-rich, circular inclusions, located along healed fractures, which usually appear to cut across trails containing inclusion types 1 and 2. Crushing studies in immersion oil under a microscope showed no volumetric expansion of contents implying that these inclusions are aqueous rather than CO₂–CH₄–N₂-rich fluids. Thermometric analysis could not be carried out due to the small size and lack of a vapour bubble.

All three major inclusion types are ubiquitous

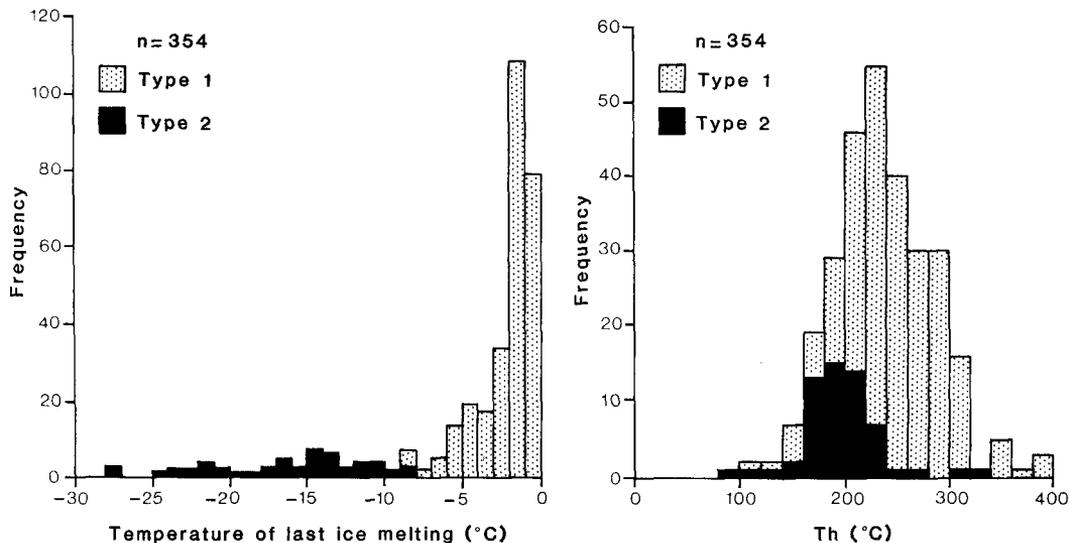


Fig. 4. Histograms showing the distribution of last ice melting (T_{lm}) and homogenization temperatures (T_h) for fluid inclusions in all rock types from Aclare and Monaughrim. Histograms are superimposed, not added.

in both the granites and pegmatites and there appears to be no systematic variation in their distributions between barren and mineralized pegmatites, and the associated granites. Two further inclusion types representing less than 0.1% of the total inclusion population were also occasionally observed. The first, a liquid-rich type coexisting with type 1 and 2 inclusions has a daughter mineral tentatively identified as halite. Their scarcity precluded any attempt to determine their T_h and salinity range and only one successful run was completed, T_s (dissolution of daughter mineral) = 310 °C and $T_h > 500$ °C, but leakage was suspected. The second group appears to contain H_2O and CO_2 . The CO_2 is a very minor component but gas-clathrate has been tentatively observed in a few inclusions. Inclusion types 1 and 2 comprise over 90% of the inclusions and the thermometric data for them presented in Fig. 4 is discussed below.

Discussion and interpretation of results

Significance of thermometric data from secondary fluid inclusions

As previously stated, one of the major problems in the interpretation of fluid-inclusion data from quartz in granitic rocks is the difficulty in identifying primary quartz with primary inclusions. Post-magmatic recrystallization and super-

imposition of many generations of secondary inclusions appears to be the rule rather than the exception (Tuttle, 1949; Rankin and Alderton, 1983 and 1985; Pêcher *et al.*, 1985). Recent studies by London (1985) on the apparently coeval quartz and spodumene from the Tanco pegmatite have further shown that, even if well-formed primary inclusions are present, the results from the two minerals may be incompatible due to preferential subsolidus recrystallization of quartz. Faced with these problems and the lack of paragenetic evidence to suggest that any of the inclusions studied in SE Ireland are primary (*sensu stricto*), it may be argued that the fluid-inclusion data are of little value in understanding late-magmatic and hydrothermal processes in these rocks. However, as discussed below, it is possible to infer a likely composition and P - T conditions of formation for early fluids represented by type 1 inclusions based on an evaluation of paired T_h -salinity data (summarized in Fig. 5) and the superimposition of pertinent isochores on an appropriate experimental phase diagram.

Relationship between type 1 and type 2 inclusions

Type 2 inclusion trails appear to cross-cut type 1 inclusion trails and, when the data are considered as bivariate T_h -salinity plots, it is evident that the inclusion types do indeed form separate trends or groupings (Fig. 5). Hence we can corroborate the initial microscope observations that at

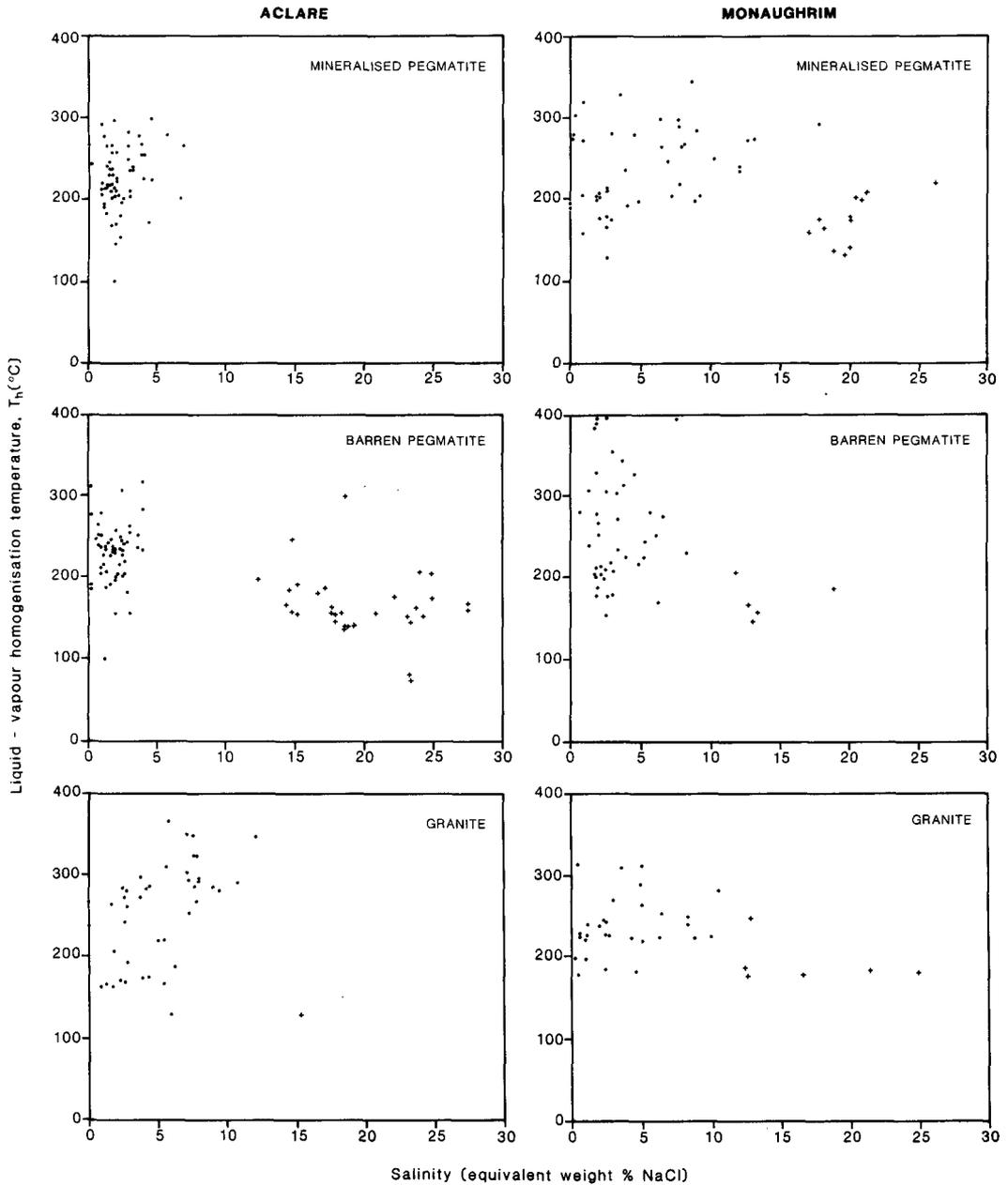


Fig. 5. Salinity- T_h plots for type 1 (circles) and 2 (crosses) fluid inclusions from mineralized and barren pegmatites and granites from Aclare and Monaughrim.

least two distinct fluid regimes have affected both the granites and their associated pegmatites. Type 1 inclusions form a separate group showing a dec-

reasing temperature (T_h 400 down to 100 °C) and salinity (10-0 eq.wt.% NaCl) whereas type 2 inclusions form a group with a relatively narrow

range of T_h and moderate to high salinities (characteristically 11 to >23 eq. wt. % NaCl).

Interpretation of paired T_h -salinity data

The two main groupings of type 1 and type 2 inclusions (Fig. 5) are believed to represent two dominant fluid regimes associated with the pegmatites and granites at different times. Paragenetically, type 1 inclusions are earlier than the type 2 inclusions and will be considered separately in the foregoing discussion.

Type 1 fluids. In the Aclare pegmatites, type 1 fluids show a wide range of homogenization temperatures (mainly 100–320 °C) but a quite narrow range of salinities (0–7 eq. wt. % NaCl). The spread of T_h data could, in part, be due to necking down of the inclusions. However, an alternative explanation favoured here (see also Rankin and Alderton, 1985, and Shepherd *et al.*, 1985b) is that the spread of fluid-inclusion thermometric data could be the result of progressive cooling and entrapment of an early high-temperature (>300 °C) fluid with a more or less fixed salinity of the order of 5–10 eq. wt. % NaCl. Type 1 fluids associated with the Aclare granite show a similar cooling trend, but from higher overall temperatures (up to 350 °C) and salinities (up to about 13 eq. wt. % NaCl) and dilution down to fluids with 0.5 eq. wt. % NaCl. This trend is interpreted in terms of a mixing model involving a high-temperature (>300 °C), moderately saline fluid and a lower temperature, low-salinity fluid. Similar trends have been noted for the mineralized veins and host granites in many parts of the Cornubian batholith (Rankin and Alderton, 1985, and Shepherd *et al.*, 1985a) where the low-temperature and low-salinity fluids are believed to represent dominantly heated groundwaters with low salt contents (meteoric fluid), and the higher temperature, higher salinity fluids are thought to represent early hydrothermal fluids perhaps directly evolved from the cooling granite magma.

Type 1 inclusions from all Monaghrim samples display similar cooling and dilution trends to those observed from the Aclare samples. In detail, however, the trends for different sample types from these two areas show minor variations. These subtle differences do not appear to reflect systematic variations. Whilst, for example, the spread of salinities for the mineralized Monaghrim pegmatite and Monaghrim and Aclare granites are closely comparable, the barren Monaghrim pegmatite shows a much closer grouping of salinities which is more compatible with the Aclare barren and mineralized pegmatites.

In summary, by considering the combined data for all type 1 inclusions, and by analogy with

results for the Cornubian granites (*op. cit.*), the type 1 fluids associated with the Leinster granites are thought to represent an early high-temperature, moderate-salinity fluid which underwent progressive cooling and some dilution on mixing with a separate, cooler fluid. Therefore the higher temperature and higher salinity type 1 fluid inclusions in all Leinster samples should approach, although not necessarily attain, the composition and properties of these early, possibly magmatic, fluids. An upper T_h value of 325–400 °C and a salinity of approximately 5–10 equivalent wt. % NaCl (Figs. 4 and 5) is a reasonable approximation of the characteristics of this early fluid in all rock types and will be used later to construct an isochore in order to trace the likely P - T path of the pegmatites and to explore the possibility that this fluid was derived directly from the cooling granite magma.

Type 2 fluids. Although type 2 inclusions have been observed in all samples, paired T_h -salinity data from the mineralized Aclare pegmatite are not available, and for the granite is limited to only one measurement. For the remaining samples, type 2 inclusions form a distinctive grouping with each sample showing a narrow range of homogenization temperatures, typically around 150 °C, but wider spread of salinities from about 11 to >23 eq. wt. % NaCl. We interpret these as mixing trends involving high-salinity/low-temperature fluid, and a much lower salinity fluid of comparable low temperature (most likely to be heated groundwater).

The high salinities and positions of type 2 inclusions on the T_h -salinity plots are very similar to the trends of late-stage fluid inclusions associated with the Cornubian granites (Rankin and Alderton, 1985, and Shepherd *et al.*, 1985a) in which basinal brines are believed to have played a significant role in the generation of 'cross-course' Pb-Zn-fluorite mineralization in SW England. We believe that type 2 inclusions in the Leinster pegmatites are perhaps similarly the result of influx of waters held within the surrounding metamorphic rocks. It is also tempting to suggest that, by analogy with SW England, these brines are perhaps related to comparable base metal mineralization which is found 40 km to the north of the Leinster pegmatite belt e.g. Glendalough (Fig. 1). It is conjectural as to whether influx of this fluid could have taken place at an early or late stage in the history of the granite.

The fluid represented by the type 2 inclusions from Leinster could also conceivably be responsible, at least in part, for subsolidus alteration of spodumene to muscovite and albite with a concomitant release of lithium (*cf.* Scoon, 1978;

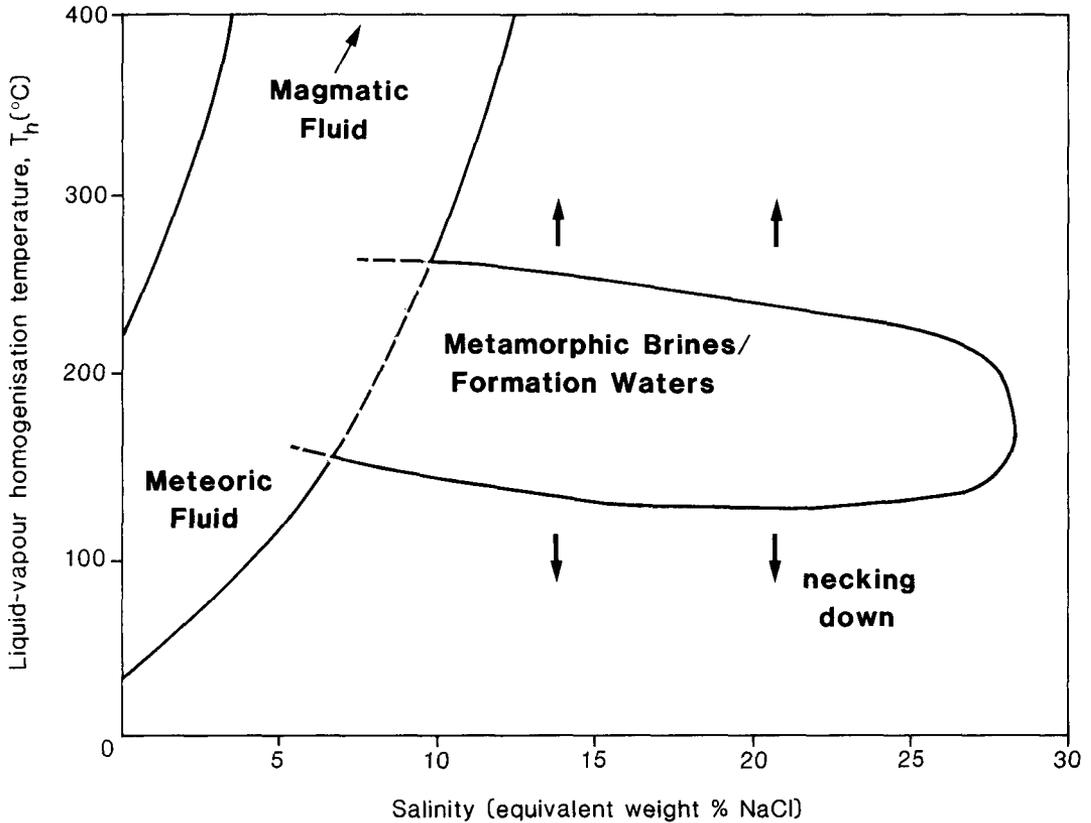


Fig. 6. Schematic salinity- T_h plot based on the model NaCl-H₂O system for fluid inclusions in quartz from the Leinster pegmatites and granites.

London and Burt, 1982). Release of lithium during the interaction of granite with basinal brines of the composition described above has also been proposed by Rankin and Graham (1988) to account for the high lithium content of the fluids in the Alston block of the Pennine Orefield. Postulated origins for the three end-member fluids in the Leinster pegmatites are summarized in Fig. 6. Simple mixing and cooling of these end-member fluids in the manner shown in Fig. 6 can account for the spread and limited necking-down of all the data on T_h -salinity plots presented in Fig. 5. There is no fluid-inclusion evidence for the co-existence of gas-rich and liquid-rich inclusions indicative of boiling in the Leinster samples.

P-T-X evolution of the pegmatites

A *P-T* diagram has been constructed showing the phase boundaries of the LiAlSiO₄-SiO₂-H₂O system (London, 1984) and isochores for type 1 fluid inclusions with salinities of 5–10 wt. % NaCl,

homogenizing at 250, 325 and 400 °C, from data in Potter and Brown (1977) and Roedder and Bodnar (1980). Isochores for inclusions homogenizing at 325 and 400 °C were chosen because these represent the earliest formed (possibly magmatic) fluids present in the samples (see above for discussion). A T_h of 250 °C was used because it is the approximate average for all type 1 fluid inclusions (Fig. 5). In addition, a *P-T* plot of the solidi for a water-saturated biotite-quartz-monzonite (Piwinski and Wyllie, 1970) with a modal composition and chemistry very similar to that of the bulk of the Leinster granite, and a biotite-hornblende granodiorite (Burnham, 1979) are plotted on the phase diagram of the system 80% Quartz-20% Eucryptite (London, 1984). The shaded area between the two solidi represents the approximate range of solidi for granite varieties encountered within the Leinster granite (Brück and O'Connor, 1977; Luecke, 1981; and Sweetman, 1988). The isochores for our postulated late-

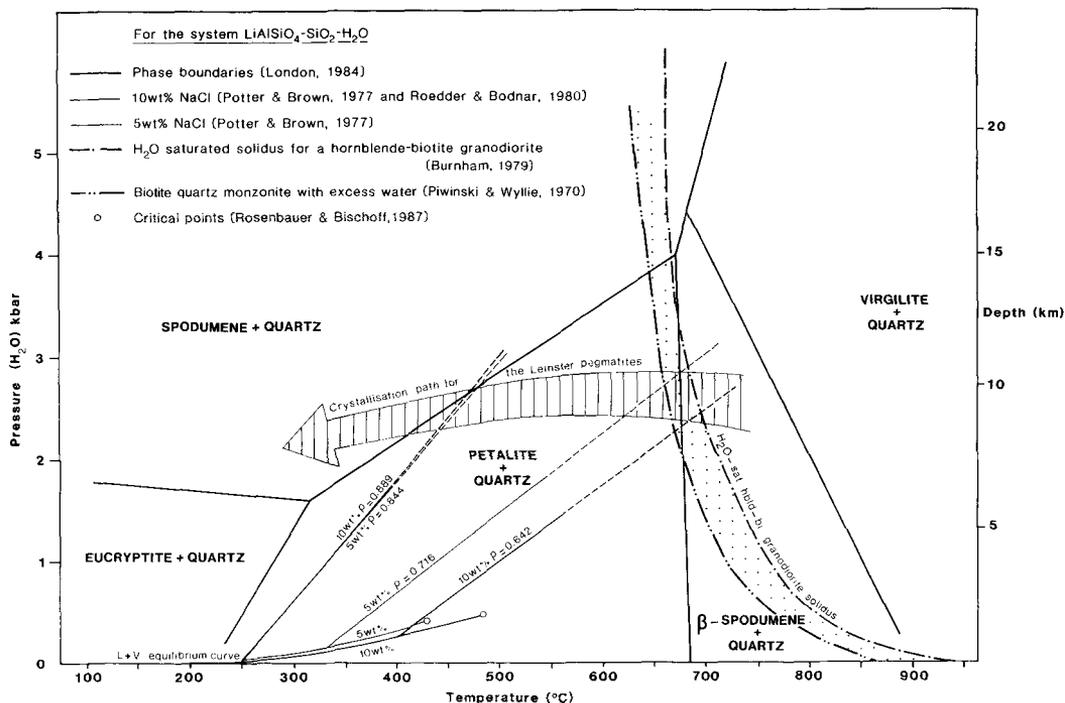


Fig. 7. P - T plot showing phase boundaries in the system LiAlSiO_4 - SiO_2 - H_2O , liquid-vapour equilibrium curves and isochores (densities given) for 5 and 10 wt. % NaCl solutions for Leinster type 1 fluid inclusions homogenizing at 250, 325 and 400 °C. Shaded area between the two solids represents the range of solids for granite varieties encountered within the Leinster granite. The cross-hatched area represents the postulated crystallization path for the Leinster lithium pegmatites. Depths corresponding to lithostatic pressure ($\rho = 2700 \text{ kgm}^{-3}$) are shown on the right hand side of the diagram.

magmatic/early-hydrothermal fluid intersect the solidi region at 2.5 kbar and a temperature of around 675 °C (Fig. 7). Presumably, after the granite had nearly completely solidified, a pegmatitic fluid developed and cooled. The inferred P - T conditions for this fluid are entirely acceptable on local geological grounds and on the basis of the accepted emplacement levels for lithium pegmatites in general (Černý, 1982). For the Leinster area, a pressure of 2.5 kbar corresponds to a depth of about 9 km, so under lithostatic conditions the data are consistent with the generation of a late-magmatic/early-hydrothermal fluid. It is apparent that the fluid inclusions with T_h values of around 250 °C and salinities of 5–10 equivalent wt. % NaCl do not simply represent higher-temperature fluids generated at greater pressures because their isochores would not intersect the biotite-quartz monzonite solidus until 650 °C and a pressure of 4.9 kbar which corresponds to depth of around 20 km (Fig. 7). This estimate of depth is clearly unreasonable for the low-medium-grade

metamorphic environment hosting the pegmatites (McArdle, 1981; McArdle and Kennedy, 1985). Furthermore, the accepted depth for formation of lithium pegmatites in general is of the order of 3.5–7 km (Černý, 1982). Initial cooling of the granite-derived fluid was under approximately isobaric conditions, thus allowing it to move through the petalite field into the spodumene field. Petalite has not been identified in the pegmatites, but a fine-grained intergrowth of spodumene and quartz may represent the breakdown products of petalite. A similar intergrowth, termed 'sqi', has been noted at Tanco (Černý and Ferguson, 1982, and London, 1986) where it is interpreted in a similar way. Hence petalite may have crystallized at some stage at Leinster but has subsequently recrystallized to 'sqi'. Continued cooling with an accompanying pressure reduction perhaps as the fluid mixed with cooler groundwaters would cause the fluid to move into the eucryptite stability field but since eucryptite is not present, a minimum pressure for the development

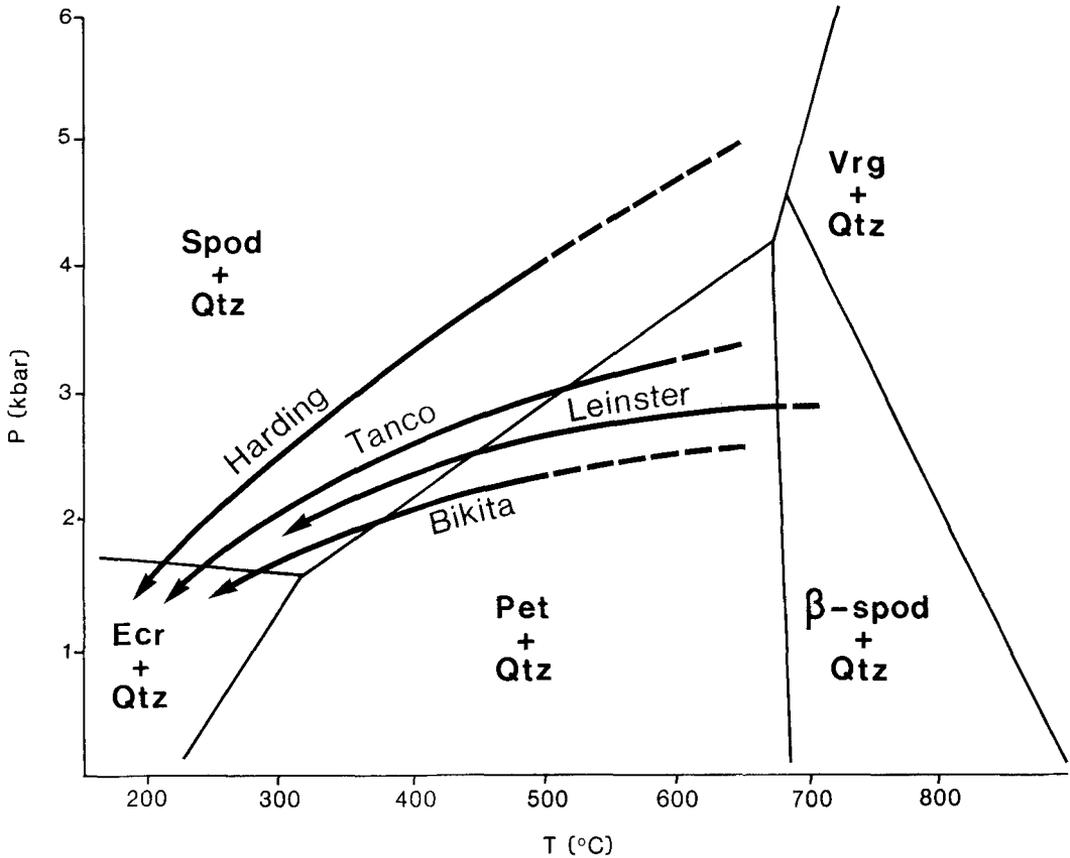


Fig. 8. Comparative P - T plot showing crystallization paths of Leinster pegmatites compared with other lithium-bearing pegmatites (London, 1986). Phase boundaries as shown in Fig. 7.

of the pegmatites may be postulated as being 1.7 kbar, equivalent to approximately 6 km depth. An influx of the meteoric water at an earlier stage in the development of the pegmatites is ruled out because an accompanying decrease in pressure resulting from the opening up of fractures would define an evolutionary trend for the fluid which would not permit the crystallization of any spodumene, the only significant lithium mineral present in the pegmatite dykes. Consequently meteoric fluid infiltration during crystallization must have been minimal and probably only occurred in the final stages, possibly accounting for the drop in pressure shown in Fig. 7 and mentioned above. The drop in pressure allowed complete crystallization within the spodumene field by around 250–300 °C and a minimum pressure of about 1.9 kbar (approximately 7 km depth). The postulated evolutionary trend is similar to that of Tanco and Bikita pegmatites (Fig. 8).

Further work on stable isotopes is in progress to further supplement our data and to test the hypothesis that early hydrothermal fluids, meteoric waters and metamorphic/formation waters have interacted not only with the lithium pegmatites but also with the granites and barren pegmatites.

Conclusions

Inclusion data coupled with phase relationships and textural features have permitted an insight into the crystallization of the internally zoned, spodumene-bearing and barren pegmatites associated with the Leinster granite. Two main fluid inclusion types (1 and 2), both two phase $L + V$ (aq) have been recognized within quartz from the lithium pegmatites and their associated granites and barren pegmatites.

Thermometric analyses of inclusion types 1 and 2 has revealed two main groupings on bivariate

T_h -salinity plots. *PVTX* modelling of early type 1 fluids in conjunction with appropriate phase boundaries in the system $\text{LiAlSi}_3\text{O}_8\text{-SiO}_2\text{-H}_2\text{O}$ has shown that the thermometric data are compatible with the generation of a magmatically derived fluid with a salinity around 5–10 wt. % NaCl from a granitic parent at about 2.5 kbar and 675 °C. In the lithium pegmatites this fluid cooled isobarically to just below 450 °C and 2.5 kbar where it entered the spodumene stability field. Eucryptite is notably absent as a primary or secondary phase in the pegmatites. Therefore a minimum pressure of 1.7 kbar can be postulated for the crystallization of the pegmatites, a pressure which corresponds to a depth of approximately 6 km in the crust. Thus, type 1 inclusions are directly related to the generation of late-stage pegmatites associated with the Leinster granite. Whilst we generally favour a late-magmatic/early-hydrothermal origin for higher temperature type 1 fluid inclusions, we cannot entirely rule out the possibility that they represent post-crystallization metamorphic fluids related to post-emplacement metamorphic events. However, one might expect a larger component of CO_2 and/or CH_4 in the inclusions if this were the case (Crawford, 1981, and Touret, 1981).

A separate and later fluid regime is characterized by the low-temperature, moderate-to high-salinity, type 2 inclusions. We believe that these represent fluids held in the associated metavolcanics and sediments, and remobilised during a later period of hydrothermal activity after the pegmatites had solidified. These fluids may have been related to or responsible for associated Pb–Zn–fluorite mineralization in the area and also may have contributed to spodumene alteration to muscovite and albite.

Comparison of the evolutionary paths of the Leinster pegmatites with those of other lithium-bearing pegmatites indicates that they have followed very similar P – T paths despite the relatively simple mineralogy, morphology and fluid-inclusion populations of the Leinster pegmatites (Fig. 8). We have been unable to identify a specific fluid inclusion type associated solely with the mineralized pegmatites. However, all these data are compatible with a magmatic, as opposed to metamorphic, origin for both mineralized and barren pegmatites associated with the Leinster granite.

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References

- Alderton, D. H. M. and Rankin, A. H. (1982) The character and evolution of hydrothermal fluids associated with the kaolinised St. Austell granite. *J. Geol. Soc. Lond.* **140**, 297–309.
- Boyarskaya, R. V., Dolomanova, Y. I., Nosik, L. P., and Fadyukov, Y. M. (1977) Morphology and chemical compositions of inclusions of parent solutions in reticulate quartz from pegmatites of Volhyn; data of scanning electron microscopy and mass spectrometry. *Abstr. in Fluid inclusion abstracts. Proc. COFFI 10*, 34.
- Brindley, J. C. (1957) Basement rocks. In *A View of Ireland* (J. Meanan and D. A. Webb, eds.), Dublin, 15–22.
- (1973) The Structural setting of the Leinster granite, Ireland. *Sci. proc. R. Dublin Soc.*, Ser. A5, 27–36.
- Brück, P. M. (1974) Granite varieties and structures of the Northern and Upper Liffey Valley Units of the Leinster batholith. *Bull. Geol. Surv. Ireland*, **1**, 381–94.
- and O'Connor, P. J. (1977) The Leinster batholith: geology and geochemistry of the northern units. *Ibid.* **2**, 107–42.
- Colthurst, J. R. J., Feely, M., Gardiner, P. R. R., Penney, S. R., Reeves, T. J., Shannon, P. M., Smith, D. G., and Vanguetaine, M. (1979) Southeast Ireland: Lower Palaeozoic stratigraphy and depositional history. In *The Caledonides of the British Isles—Reviewed* (A. L. Harris, C. H. Holland and B. E. Leake, eds.) Scottish Academic Press, 533–44.
- Burnham, C. W. (1979) Magmas and hydrothermal fluids. In *Geochemistry of hydrothermal ore deposits* (Barnes, H. L., ed.) Wiley and Son, New York, 71–136.
- Cameron, E. N., Jahns, R. H., McNair, A. H., and Page, L. R. (1949) *Internal structure of granitic pegmatites*. Econ. Geol. Monogr. 2.
- Černý, P. (1982) Anatomy and classification of granitic pegmatites. In *Short course in granitic pegmatites in science and industry* (Černý, P., ed.). Min. Assoc. Can. **12**, 1–40.
- and Ferguson, R. B. (1982). The Tanco pegmatite at Bernic Lake, Manitoba. IV. Petalite and spodumene relations. *Can. Mineral.* **11**, 660–78.
- Chrystoulis, S. L. and Rankin, A. H. (1988) Decrepito-

- metry of fluid inclusions in quartz from the Guadaluza granite of Mexico. *Mineral. Dep.* **23**, 42–9.
- Cooper, M. A. and Brück, P. M. (1983) Tectonic relationships of the Leinster granite, Ireland. *Geol. J.* **18**, 351–60.
- Crawford, M. L. (1981) Fluid inclusions in metamorphic rocks—low and medium grade. *Short course in fluid inclusions: applications to petrology* (Hollister, L. S. and Crawford, M. L., eds.). *Min. Assoc. Can.* **6**, 157–81.
- Elsdon, R. and Kennan, P. S. (1982) Age of sulphide deposits on the margin of the Leinster granite, Ireland. In *Metallization associated with acid magmatism* **6** (Evans, A. M., ed.) Wiley, Chichester, 85–9.
- Gallagher, V. (1987) *Tourmaline-bearing rocks and granite related metallogenesis in SE Ireland*. Unpubl. Ph.D. thesis, Nat. Univ. Ireland.
- Hall, D. L., Sterner, S. M., and Bodnar, R. J. (1988) Freezing point depression of NaCl–KCl–H₂O solutions. *Econ. Geol.* **83**, 197–202.
- Halls, C. (1987) A Mechanistic approach to the paragenetic interpretation of mineral lodes in Cornwall. *Proc. Ussher Soc.* **6**, 548–54.
- Kennan, P. S., McArdle, P., Williams, F. M., and Doyle, E. (1986) A Review of metal deposits associated with the Leinster granite, SE Ireland and a model for their genesis. In *Geology and genesis of mineral deposits in Ireland* (Andrews, C. J. et al., eds.), Irish Assoc. Econ. Geol., Dublin, 201–10.
- Kesler, T. L. (1978) Raw lithium supplies. *Mining Engin.* **30**, 283–4.
- Konnerup-Madsen, J. (1977) Composition and microthermometry of fluid inclusions in the Kleivan granite, south Norway. *Am. J. Sci.* **277**, 673–96.
- (1979) Fluid inclusions in quartz from deep-seated granitic intrusions, south Norway. *Lithos*, **12**, 13–23.
- Kunasz, I. (1982) Foote mineral company—Kings Mountain Operation. In *Short course in granitic pegmatites in science and industry* (Černý, P., ed.), *Min. Assoc. Can.* **12**, 505–12.
- London, D. (1984) Experimental phase equilibria in the system LiAlSiO₄–SiO₂–H₂O: a petrogenetic grid for lithium-rich pegmatites. *Am. Mineral.* **69**, 995–1004.
- (1985) Origin and significance of inclusions in quartz: a cautionary example from the Tanco pegmatite, Manitoba. *Econ. Geol.* **80**, 1988–95.
- (1986) Magmatic–hydrothermal transition in the Tanco rare-element pegmatite: evidence from fluid inclusions and phase-equilibrium experiments. *Am. Mineral.* **71**, 376–95.
- and Burt, D. M. (1982) Alteration of spodumene, montebrazite and lithiophilite in pegmatites of the White Picacho district, Arizona. *Ibid.* **67**, 97–113.
- Luecke, W. (1981) Lithium pegmatites in the Leinster granite (Southeast Ireland). *Chem. Geol.* **34**, 195–233.
- McArdle, P. (1981) The Country rocks flanking the Leinster granite between Aghrim and Ballymurphy. *Bull. Geol. Surv. Ireland*, **3**, 85–95.
- and Kennedy, M. J. (1985) The East Carlow deformation zone and its regional implications. *Ibid.* **3**, 237–55.
- Naumov, G. B., Kovalenko, V. I., Ivanov, G. F., and Vladykin, N. B. (1977) Genesis of topaz according to the data on microinclusions. *Geochem. Internat.* **14**, 1–8.
- O'Connor, P. J. and Brück, P. M. (1978) Age and origin of the Leinster granite. *J. Earth Sci., R. Dubl. Soc.* **1**, 105–13.
- Olsen, K. I. and Griffin, W. L. (1984a) Fluid inclusion studies of the Drammen granite, Oslo paleorift, Norway. I. Microthermometry. *Contrib. Mineral. Petrol.* **87**, 1–14.
- (1984b) Fluid inclusion studies of the Drammen granite, Oslo paleorift, Norway. II. Gas-and leachate analyses of mirolitic quartz. *Ibid.* **87**, 15–23.
- Pêcher, A., Lespinasse, M., and Leroy, J. (1985) Relation between fluid inclusion trails and regional stress field: a tool for fluid chronology. The example of an intragranitic uranium ore deposit, Northwest Massif Central, France. *Lithos*, **18**, 229–37.
- Piwinskii, A. J. and Wyllie, P. J. (1970) Experimental studies on igneous rock series: felsic body suite from the Needle Point pluton, Wallowa batholith, Oregon. *J. Geol.* **78**, 52–76.
- Potter, R. W. and Brown, D. L. (1977) The volumetric properties of aqueous sodium chloride solutions from 0 to 500 °C at pressures up to 2000 bars based on a regression of available data in the literature. *U.S. Geol. Surv. Bull.* 1421–C.
- Clynne, M. A., and Brown, D. L. (1978) Freezing point depression of aqueous sodium chloride solutions. *Econ. Geol.* **73**, 284–5.
- Rankin, A. H. and Alderton, D. H. M. (1983) Fluid inclusion petrography of SW England granites and its potential in mineral exploration. *Mineral. Dep.* **18**, 335–47.
- (1985) Fluids in granites from southwest England. In *High heat producing (HHP) granites, hydrothermal circulation and ore genesis*. *Inst. Min. Metall.*, 287–300.
- and Criddle, A. J. (1985) Mineralizing fluids and metastable low-temperature inclusion brines at Llanharry iron deposit, South Wales. *Trans. Inst. Min. Metall.* **94**, B126–32.
- and Graham, M. J. (1988) Na, K and Li contents of mineralizing fluids in the North Pennines orefield and their genetic significance. *Ibid.* **97**, B99–107.
- Roedder, E. (1971) Metastability in fluid inclusions. *Proc. IMA-IGOD meetings 1970*, 327–34. *Spec. Iss. Soc. Min. Geol. Japan.*
- (1984) *Fluid Inclusions. Reviews in mineralogy* **12**, *Min. Soc. Am.*, 644pp.
- and Bodnar, R. J. (1980) Geologic pressure determinations from fluid inclusion studies. *Ann. Rev. Earth Planet. Sci.* **8**, 263–301.
- Rosenbauer, R. J. and Bischoff, J. L. (1987) Pressure–composition relations for coexisting gases and liquids and the critical points in the system NaCl–H₂O at 450, 475 and 500 °C. *Geochim. Cosmochim. Acta*, **51**, 2349–54.
- Rossovskii, L. N. (1981) Rare-element pegmatites with precious stones and conditions of their formation (Hindu Kush). *Int. Geol. Rev.* **23**, 1312–20.
- Scoon, R. N. (1978) *Lithium pegmatites in the Leinster*

- granites of south-east Ireland*. Unpub. M.Sc. thesis, Univ. Coll. Cardiff.
- Shepherd, T. J., Miller, M. F., Scrivener, R. C., and Darbyshire, D. P. F. (1985a) Hydrothermal fluid evolution in relation to mineralization in southwest England with special reference to the Dartmoor/Bodmin area. In *High heat producing (HHP) granites, hydrothermal circulation and ore genesis*. Inst. Min. Metall., 345–64.
- Rankin, A. H., and Alderton, D. H. M. (1985b) *A practical guide to fluid inclusion studies*. Blackie, London, 239pp.
- Steiger, R. (1977) Prospecting for lithium and tungsten in Ireland. In *Prospecting in areas of glaciated terrain, Helsinki*. Inst. Min. Metall., 14–24.
- and von Knorring, O. (1974) A lithium pegmatite belt in Ireland. *J. Earth Sci. Leeds Geol. Assoc.* **8**, 433–43.
- Sweetman, T. (1988) The geochemistry of the Blackstairs Unit of the Leinster granite, Ireland. *J. Geol. Soc.* **144**, 971–84.
- Thomson, T. (1836) *Outlines of mineralogy, geology and mineral analysis*, Vols I-II, London.
- Touret, J. (1981) Fluid inclusions in high grade metamorphic rocks. *Short course in fluid inclusions: applications to petrology* (Hollister, L. S. and Crawford, M. L., eds.). Min. Assoc. Can. **6**, 182–208.
- Tuttle, O. F. (1949) Structural petrology of planes of liquid inclusions. *J. Geol.* **57**, 331–56.
- Weisbrod, A. and Poty, B. (1975) Thermodynamics and geochemistry of the hydrothermal evolution of the Mayres pegmatite. *Pétrologie*, **1**, 1–16 and 89–102.
- Williams, F. M. and Kennan, P. S. (1983) Stable isotope studies of sulphide mineralization on the Leinster granite margin and some observations on its relationship to cotecule and tourmalinite rocks in the aureole. *Mineral. Dep.* **18**, 399–410.
- Zakharchenko, A. I. (1971). Time and physicochemical conditions of mobilisation, transport and precipitation of tungsten and tin in post magmatic processes. Abstract in *Fluid inclusion abstracts, Proc. COFFI* **6**, 191–4.

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