Earth and Environmental Science Transactions of the Royal Society of Edinburgh, **101**, 53–66, 2010

Fluid inclusions in Irish granite quartz: monitors of fluids trapped in the onshore Irish Massif

J. Conliffe[1,2] and M. Feely[1]

[1] Department of Earth and Ocean Sciences, National University of Ireland, Galway, Ireland
Email: martin.feely@nuigalway.ie

[2] Present address: Department of Earth Sciences, Memorial University of Newfoundland, St John's, NL, Canada
Email: jamesconliffe@mun.ca

ABSTRACT: Fluid inclusion studies of granite quartz provide an opportunity to study fluid flow associated with igneous activity and post-emplacement fluid processes. This study presents new fluid inclusion data from the late Caledonian Donegal granites and Newry granodiorite, and the Tertiary Mourne Mountains granite in Ireland, which identify three distinct fluids. Aqueous-carbonic fluids (Type 1) have been recorded in late Caledonian granites with a significant mantle component (Newry granodiorite and the Ardara and Thorr granites in Donegal). These fluids represent late-magmatic fluids trapped at high temperatures (up to 575 °C), and the ultimate source of these carbonic fluids is linked to sub-lithospheric processes during the Caledonian orogeny. The dominant fluid type (Type 2) in late Caledonian granites is a $H_2O+NaCl\pm KCl$ fluid which may be related to thermal convection cells around granite bodies and/or to regional scale influx of surface derived fluids at the end of the Caledonian orogeny. High salinity $NaCl–CaCl_2$ fluids (Type 3) overprint quartz in the Ardara granite in Donegal, and in the Newry granodiorite, and are interpreted to represent basinal brines, sourced in overlying sedimentary basins, which circulated through the crystalline basement during a period of crustal extension (possibly during the Carboniferous or the Triassic). Fluid inclusion studies of the Tertiary Mourne Mountains granites have identified only Type 2 fluids related to thermal convection cells, consistent with stable isotope evidence, which indicates that this younger granite is unaffected by regional-scale fluid influxes.

KEY WORDS: Caledonian granites, Tertiary granites

Understanding the nature and relative timing of fluid influxes in the upper crust is one of the fundamental goals in Earth Science. Fluid influxes in the upper continental crust may be related to igneous activity (Rankin & Alderton 1985; Möller *et al.* 1997) or to the infiltration of surface derived fluids into crystalline basement (Möller *et al.* 1997; Yardley *et al.* 2000; Gleeson *et al.* 2003) and these influxes impact on a variety of geological processes, including heat transfer, alteration of rock chemistry, diagenesis and accumulation of economic oil, gas and metal deposits. Granite intrusions represent a significant component of the upper continental crust and therefore fluid inclusion studies of granite plutons provide an opportunity to study fluids associated with both igneous activity and post-emplacement fluid processes linked to certain tectonic settings.

This study presents new petrographic and microthermometric data from granite quartz hosted by the Donegal, Newry and Mourne Mountains granites, and is integrated with microthermometric data from the Galway granites (Gallagher *et al.* 1992; O'Reilly *et al.* 1997a; Feely *et al.* 2007), Oughterard granite (Feely *et al.* 2006), Kentstown granite (O'Reilly *et al.* 1997b) and the Leinster granite (Whitworth & Rankin 1989; Moran 2003). The composition, possible sources and timing of these fluid influxes are characterised and the results are discussed in the context of fluid influxes in the Irish upper continental crust.

1. Geological background

The onshore Irish massif provides an ideal opportunity to study fluid inclusions in quartz hosted by granites emplaced between ~460 Ma and ~60 Ma (Fig. 1). The majority of Irish granites are associated with the Caledonian orogeny (~470 Ma to 380 Ma – Freidrich *et al.* 1999; Feely *et al.* 2003, 2007) and have been divided into 'Older' and 'Late' granites by Read (1961). The 'Older' granites, including the Oughterard granite, are generally coeval with high grade Grampian regional metamorphism at ~470 Ma (Dewey & Mange 1999) and are S-type granites. Late Caledonian granites were emplaced 40–90 Ma later, well after peak metamorphism and towards the end of the Caledonian orogen. Although all late Caledonian granites are I-type, there are significant geochemical differences between these late Caledonian granites that in turn reflect differences in the source of granite magmas (Sweetman 1987; Crowley 1997; Atherton & Ghani 2002; Ghani & Atherton 2006). The Tertiary Mourne Mountains granites are associated with the opening of the North Atlantic during the Paleocene (~57 Ma) and are confined to the final stages of igneous activity in the British Tertiary Igneous Province (Gamble *et al.* 1999).

1.1. Donegal granites

The Donegal granites (Fig. 2a) are a suite of eight post-tectonic intrusions emplaced into a ductile shear zone (Pitcher & Berger 1972; Hutton 1982). Geochronological constraints indicate that emplacement of the Donegal granites was protracted, and occurred from *c.* 428 Ma until *c.* 400 Ma (Halliday *et al.* 1980; O'Connor *et al.* 1982, 1987; Condon *et al.* 2004). Their geology, emplacement mechanisms and geochemistry are well documented (Pitcher & Berger 1972; Hutton 1982; Ghani and

doi:10.1017/S1755691010009047

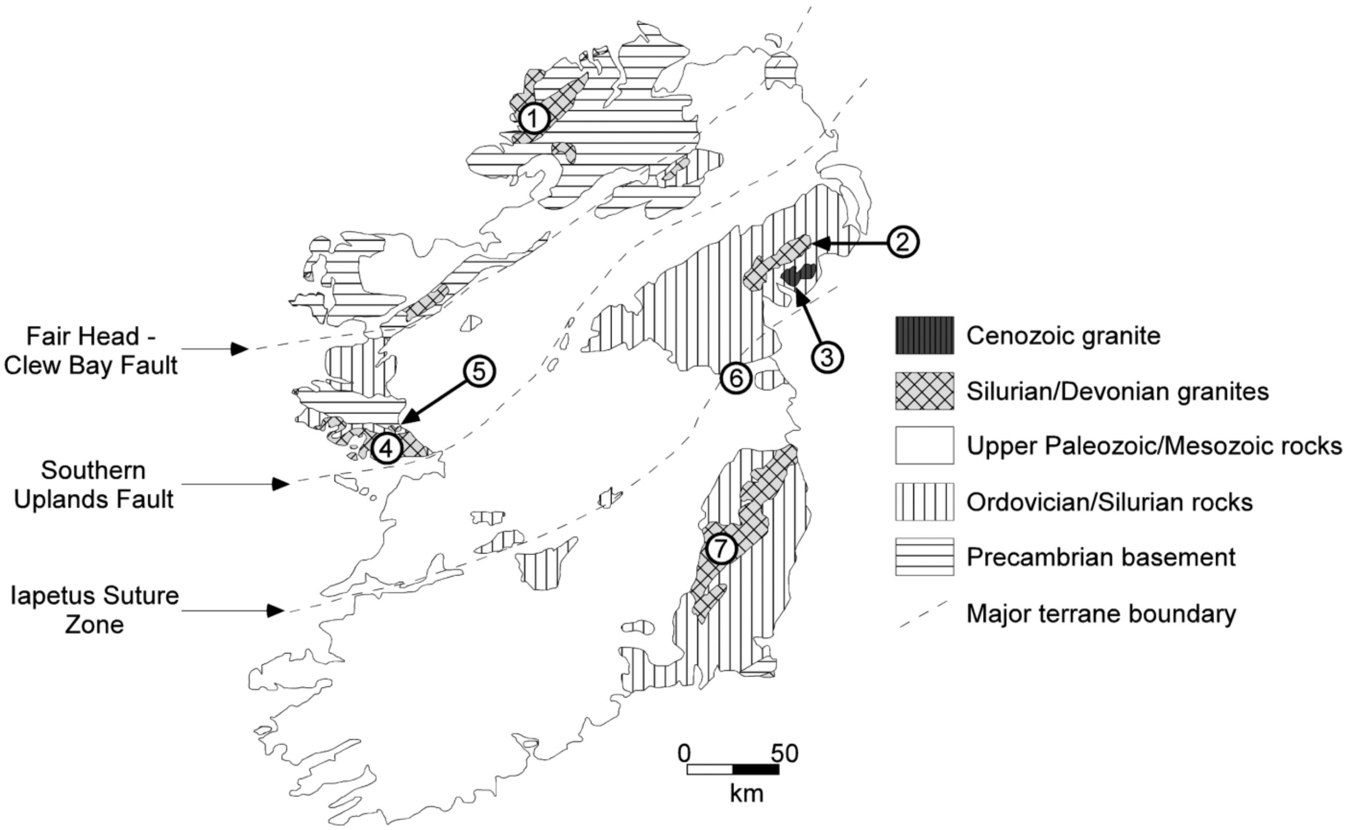

Figure 1 Geological map of Ireland showing location of granite plutons discussed in the text. 1=Donegal granites; 2=Newry granodiorite; 3=Mourne Mountains granites; 4=Galway granites; 5=Oughterard granite; 6=Kentstown granite; 7=Leinster granite.

Atherton 2006). Two chemically and isotopically distinct granite suites have been recognised (Ghani & Atherton 2006): (1) the Thorr, Ardara and Fanad suite; and (2) the Rosses and Trawenagh Bay suite. The Main Donegal granite has intermediate characteristics. Ghani & Atherton (2006) invoked a mechanism of slab breakoff in order to explain the origin of the two magmatic suites, with the former reflecting a mantle signature related to the partial melting of lamprophyric, underplated crust after slab breakoff and the latter related to the partial melting of shallower, older crust with only a minor mantle component.

1.2. Newry granodiorite

The late Caledonian Newry granodiorite (Fig. 2b) is composed of three composite granodiorite plutons and is associated with a complex of ultramafic and intermediate rocks that together constitute the Newry Igneous Complex (Meighan & Neeson 1979). The complex is cut by late Caledonian and Tertiary dykes and at the SW end by the Slieve Gullion Tertiary Complex. Zircons from the central pluton yield a provisional ^{207}Pb/^{206}Pb age of 426 ± 7 Ma, consistent with a U/Pb age of 423 ± 7 Ma determined using sensitive high-resolution ion microprobe (SHRIMP) analysis (Meighan *et al.* 2003a). Meighan & Neeson (1979) recognised several injections of magma in each granite pluton and considered that all rock types in the Newry Igneous Complex are genetically related and that the granodiorites originated by crystal fractionation of large volumes of intermediate magmas of mantle origin.

1.3. Mourne Mountains granites

The Mourne Mountains granites (Fig. 2b) form part of the British Tertiary Igneous Complex (BTIP) which developed during seafloor spreading in the North Atlantic. Gamble *et al.* (1999) reported a zircon ^{206}Pb–^{238}U age of 56·6 ± 1·4 Ma, using SHRIMP analysis. Five main granite types have been recognised in the Mourne Mountains (G1–G5), each representing a number of granite pulses (Meighan *et al.* 1984). Geochemical studies have shown the Mourne granites to be essentially highly evolved, with high Rb and low Sr abundances coupled with large negative Eu anomalies (Meighan *et al.* 1984). Stevenson *et al.* (2007) showed that the eastern portion of the Mourne Mountains granites is a laccolith based upon anisotropy of magnetic susceptibility (AMS) data. Meighan *et al.* (1984) argued that the granite magma evolved from fractionation of a basaltic magma at depth and that the most fractionated granites (G2–G4) could have been generated by the fractional crystallisation of a magma of G1 composition, with G5 representing a return to a more basic composition which therefore may not be strictly comagmatic with the other intrusions. However, the view that crystal fractionation was the only process involved in the evolution of the Mourne Mountains granites is not consistent with Sr isotope evidence, which indicates significant crustal contamination (Meighan *et al.* 1992).

2. Sampling and methodology

Thirty three samples were collected from the Donegal granites (22), Newry granodiorite (6) and Mourne Mountains granite (5). Fluid inclusion petrography and microthermometric analyses were conducted at the Geofluids Research Laboratory, National University of Ireland, Galway. Microthermometric analyses were performed on doubly polished wafers using a calibrated Linkam THMS600 heating–freezing stage. Calibration was conducted using synthetic H_2O and CO_2 fluid inclusion standards and the accuracy was ±0·2°C at −56·6°C and ±1°C at 300°C. Analytical precision, determined by replicate measurements, was ±0·1°C. Following

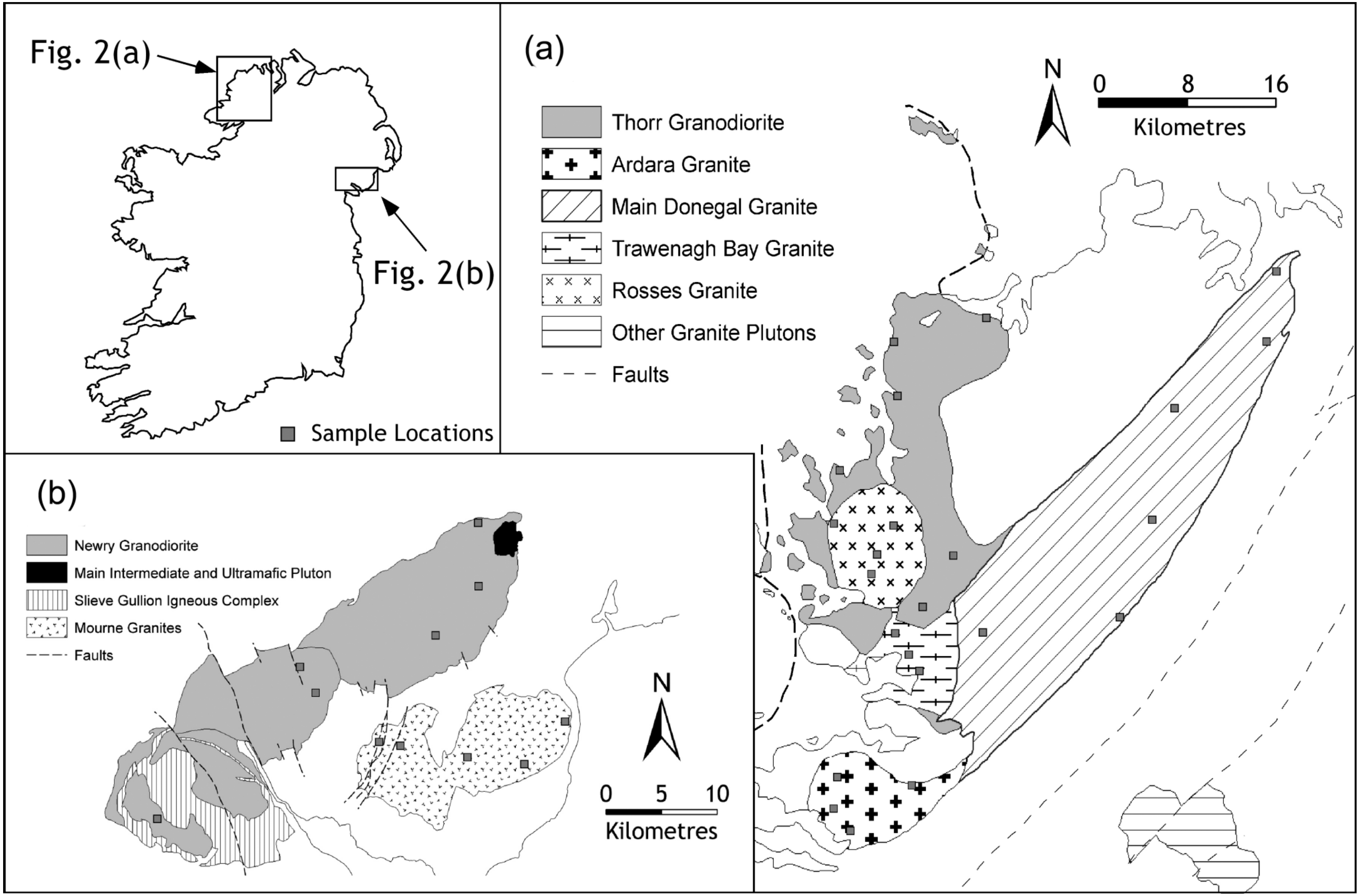

Figure 2 Geological map of the Donegal granites, Newry granodiorite and Mourne Mountains granites showing sample locations.

Table 1 Fluid inclusion microthermometric data from the Donegal granites, Newry granodiorite and Mourne Mountains granites.

Fluid inclusion type	Donegal granites		
	Thorr granite	Ardara granite	Main Donegal granite
Type 1: 5 µm to 40 µm Fill=0·37 to 0·87 occur as large isolated inclusions randomly distributed within quartz grains or occasionally in clusters. Ellipsoidal, irregular and negative-crystal shapes	$T_M\mathit{CO}_2 = -59{\cdot}8 \sim -56{\cdot}6$°C (15) $T_M\mathit{clath} = 3{\cdot}6 \sim 10{\cdot}2$°C (18) (=2·2 ~ 12 eq. wt.% NaCl) $T_H\mathit{CO}_2$ (L)=27·1 ~ 31·1°C (14) CO_2 density=0·58 ~ 0·67 g/cc T_H (L)=301 ~ 430°C (22)	$T_M\mathit{CO}_2 = -58{\cdot}1 \sim -56{\cdot}8$°C (6) $T_M\mathit{clath} = 4{\cdot}4 \sim 8{\cdot}5$°C (8) (=2·5 ~ 9·8 eq. wt.% NaCl) $T_H\mathit{CO}_2$ (L)=27·1 ~ 31·1°C (6) CO_2 density=0·7 ~ 0·81 g/cc T_H (L)=326 ~ 408°C (4)	Absent
Type 2: 5 µm to 30 µm Fill=0·56 to 0·97 occur in granite quartz in clusters and trails along annealed fractures. Ellipsoidal, irregular and negative-crystal shapes	$T_{FM} = -28{\cdot}9 \sim -19{\cdot}8$°C (31) $T_{LM} = -6{\cdot}9 \sim -0{\cdot}1$°C (150) (=0·2 ~ 10·4 eq. wt.% NaCl) T_H (L)=101 ~ 376°C (155)	$T_{FM} = -29{\cdot}8 \sim -19{\cdot}5$°C (24) $T_{LM} = -9{\cdot}7 \sim -0{\cdot}7$°C (72) (=1·2 ~ 13·6 eq. wt.% NaCl) T_H (L)=117 ~ 414°C (82)	$T_{FM} = -27{\cdot}6 \sim -19{\cdot}7$°C (45) $T_{LM} = -10{\cdot}1 \sim -0{\cdot}4$°C (152) (=0·8 ~ 14 eq. wt.% NaCl) T_H (L)=115 ~ 394°C (154)
Type 3: 5 µm to 20 µm Fill=0·85 to 0·99 occur in granite quartz in trails along annealed fractures. Ellipsoidal and irregular morphologies	Absent	$T_{FM} = -54{\cdot}4 \sim -48{\cdot}3$°C (28) $T_M\mathit{h} = -35{\cdot}2 \sim -29{\cdot}6$°C (8) $X_{NaCl} = 0{\cdot}16 \sim 0{\cdot}32$ $T_{LM} = -13{\cdot}6 \sim -6{\cdot}9$°C (22) (=10·4 ~ 17·4 eq. wt.% NaCl) T_H (L)=84 ~ 219°C (27)	Absent
Type 4: 5 µm to 10 µm Fill=0·66 to 0·83 occur in granite quartz in trails along annealed fractures. Ellipsoidal and negative crystal morphologies	Absent	Absent	Absent

Fill=degree of fill (volume aqueous/total volume @ 30°C or after homogenisation of carbonic phase for Type 1 inclusions); $T_M\mathit{CO}_2$=CO_2 melting temperature; $T_M\mathit{clath}$=clathrate melting temperature; $T_H\mathit{CO}_2$=homogenisation of carbonic phase; T_H (L)=total homogenisation temperature (to the liquid phase); T_D=temperature of decrepitation; T_{FM}=temperature of first ice melting; T_{LM}=temperature of last ice melting; T_M *h*=temperature of hydrohalite melting; X_{NaCl}=NaCl/(NaCl+$CaCl_2$); $T_H\mathit{halite}$=temperature of halite dissolution.

Table 1 *Continued.*

Fluid inclusion type	**Donegal granites**		**Newry granodiorite**	**Mourne Mountains granite**
	Rosses granite	**Trawenagh Bay granite**		
Type 1: 5 μm to 40 μm Fill=0·37 to 0·87 occur as large isolated inclusions randomly distributed within quartz grains or occasionally in clusters. Ellipsoidal, irregular and negative-crystal shapes	Absent	Absent	$T_{M}CO_{2}$= − 57·2 to − 55°C (10) $T_{M}clath$=0·7 to 8·4°C (17) (=2·7 ~ 16 eq. wt.% NaCl) $T_{H}CO_{2}$ (V)=28·6 ~ 31·1°C (7) CO_2 density=0·31 ~ 0·37 g/cc T_H (L)=301 ~ 415°C (18)	Absent
Type 2: 5 μm to 30 μm Fill=0·56 to 0·97 occur in granite quartz in clusters and trails along annealed fractures. Ellipsoidal, irregular and negative-crystal shapes	T_{FM}= − 26·2 to − 19·6°C (16) T_{LM}= − 5·6 to − 0·5°C (69) (=0·9 to 8·7 eq. wt.% NaCl) T_H (L)=54 to 408°C (71)	T_{FM}= − 26·2 to − 19·6°C (22) T_{LM}= − 6 to − 0·1°C (88) (=0·2 to 9·2 eq. wt.% NaCl) T_H (L)=83 to 373°C (89)	T_{FM}= − 28 to − 19°C (71) T_{LM}= − 7·9 to − 0·1°C (140) (=0·2 to 11·5 eq. wt.% NaCl) T_H (L)=120 to 382°C (144)	T_{FM}= − 29·1 ~ − 17·9°C (85) T_{LM}= − 14·3 ~ − 0·1°C (183) (=18·04 ~ 0·18 eq. wt.% NaCl) T_H (L)=171·4 ~ 394·4°C (180)
Type 3: 5 μm to 20 μm Fill=0·85 to 0·99 occur in granite quartz in trails along annealed fractures. Ellipsoidal and irregular morphologies	Absent	Absent	T_{FM}= − 55·7 ~ − 46·7°C (28) $T_{M}h$= − 29·1 ~ − 24·5°C (8) X_{NaCL}=0·34 ~ 0·64 T_{LM}= − 20·1 ~ − 3·5°C (22) (=22·5 ~ 5·7 eq. wt.% NaCl) T_H (L)=48 ~ 211°C (27)	Absent
Type 4: 5 μm to 10 μm Fill=0·66 to 0·83 occur in granite quartz in trails along annealed fractures. Ellipsoidal and negative crystal morphologies	Absent	Absent	Absent	T_{FM}= − 20·4°C (1) $T_{H}halite$= 217·6 ~ 265·7°C (3) (=32·5 ~ 35·3 eq. wt.% NaCl)

Fill=degree of fill (volume aqueous/total volume @ 30°C or after homogenisation of carbonic phase for Type 1 inclusions); $T_{M}CO_{2}$=CO_2 melting temperature; $T_{M}clath$=clathrate melting temperature; $T_{H}CO_{2}$=homogenisation of carbonic phase; T_H (L)=total homogenisation temperature (to the liquid phase); T_D=temperature of decrepitation; T_{FM}=temperature of first ice melting; T_{LM}=temperature of last ice melting; T_M *h*=temperature of hydrohalite melting; X_{NaCl}=NaCl/(NaCl+$CaCl_2$); $T_{H}halite$=temperature of halite dissolution.

procedures outlined by Shepherd *et al.* (1985) the temperatures of first ice melting (T_{FM}), hydrohalite melting ($T_{M}h$), last ice melting (T_{LM}) and the temperature of homogenisation (T_{H}) were measured in two-phase (liquid + vapour) inclusions hosted in quartz. In addition, the temperature of CO_2 melting ($T_{M}CO_2$), clathrate melting ($T_{M}clath$) and homogenisation of the carbonic phases ($T_{H}CO_2$) were recorded in aqueous-carbonic inclusions. Aqueous fluid salinities were calculated using T_{LM} and the equation of Bodnar (1993), and in aqueous-carbonic inclusions using $T_{M}clath$ and the software package CLATHRATES (Bakker 1997). Salinities and X_{NaCl} (wt.% NaCl/wt.% NaCl + $CaCl_2$) values for $CaCl_2$ bearing inclusions were calculated from $T_{M}h$ and T_{LM} using software by Chi & Ni (2007).

3. Results

Four main fluid inclusion types (Type 1, Type 2, Type 3 and Type 4) were recorded based on their morphology, number of phases at room temperature and their phase behaviour on cooling. Microthermometric data from all granite samples are summarised in Table 1. The majority of inclusions are hosted in trails along annealed fractures and are considered secondary in origin (Goldstein 2003).

Type 1 fluid inclusions are aqueous-carbonic, two-phase (liquid H_2O + liquid CO_2) and three-phase inclusions (liquid H_2O + liquid CO_2 + CO_2 vapour) at room temperature (~25 °C) (Fig. 3a). Type 1 fluid inclusions generally display irregular, ellipsoidal or negative crystal shapes and generally occur as isolated inclusions ranging in size from ~10 μm to 50 μm in longest dimension. Within an individual sample, they display consistent H_2O:CO_2 ratios (after homogenisation of the carbonic phase) and have similar microthermometric characteristics, indicating that they were not affected significantly by post-entrapment modification or inhomogeneous trapping.

Type 2 inclusions are the most common in all samples. They are two-phase (liquid + vapour) H_2O + NaCl ± KCl inclusions with first ice-melting temperatures in the range of − 30 °C to − 20 °C. They generally occur along annealed fractures, indicating that they are secondary in origin. In some samples the intersection of differently oriented trails suggests multiple phases of fluid infiltration. The majority of Type 2 inclusions range in size from 5 μm to 40 μm and their morphologies are ellipsoidal to irregular, with some displaying negative crystal shapes. They have a degree of fill (volume of liquid phase/total volume) of ~0·60 to 0·95 and the relative proportions of phases are consistent within individual fluid inclusion assemblages.

Type 3 inclusions are two-phase (liquid + vapour; Fig 3b) or monophase inclusions that also occur along annealed fracture planes. Rarely, intersecting trails of Type 2 and Type 3 inclusions have been recorded and in these samples Type 3 inclusions postdate Type 2 inclusions. They have moderate to high salinities and first ice-melting temperatures in the range of − 45 °C to − 55 °C, and are most likely NaCl–$CaCl_2$-rich fluids, although these low eutectic temperatures may indicate the presence of other divalent salts (e.g. $MgCl_2$, $FeCl_2$). Type 3 inclusions often have irregular shapes and generally have a higher degree of fill than Type 3 inclusions (>0·85).

Type 4 inclusions are three-phase (liquid + vapour + solid) inclusions and have only been recorded in the Mourne Mountains granite. The solid phase in Type 4 inclusions is cubic and isotropic and, based on its optical characteristics, it has been identified as halite.

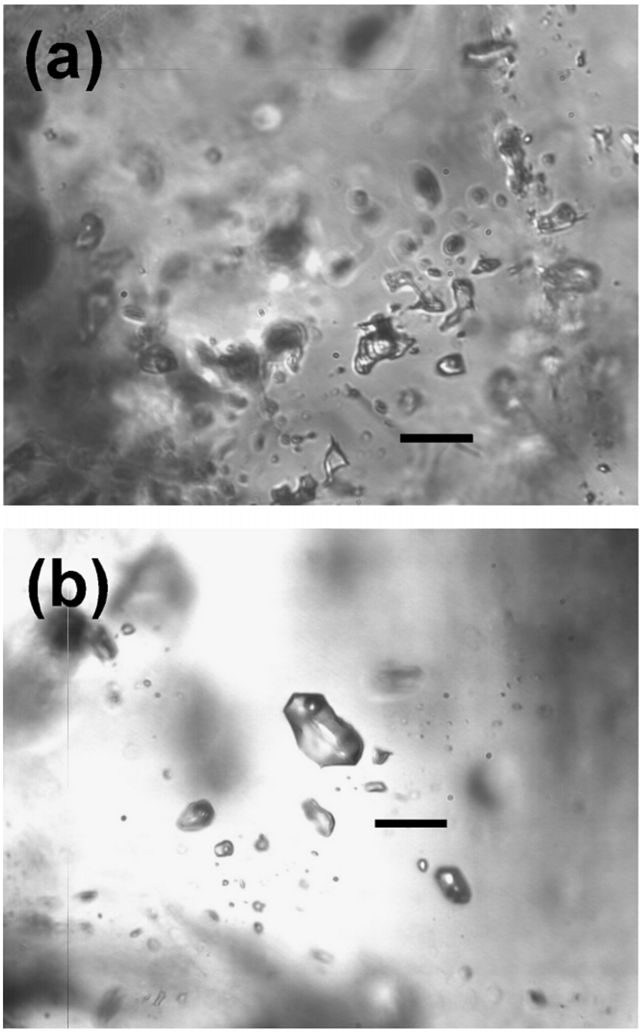

Figure 3 Photomicrograph of fluid inclusion types. Scale bar = 20μm. (a) Three phase (L_{H_2O} + L_{CO_2} + V_{CO_2}) Type 1 inclusion in the Thorr granite. (b) Two phase (L + V) aqueous Type 2 inclusions in the Mourne Mountains granites.

3.1. Donegal granites

Type 1 inclusions have only been recorded in the Thorr and Ardara granites (Fig. 4a). CO_2 melting occurs close to the eutectic point of CO_2 (− 56·6 °C), indicating that the carbonic phase in these inclusions contains little or no volatiles other than CO_2. $T_{M}clath$ yielded aqueous phase salinities of 2·2–12 eq. wt.% NaCl. Homogenisation of CO_2 (to the liquid phase) was recorded between 15·8 °C and 31·1 °C, yielding a CO_2 phase density of 0·58–0·81 g/cc. Total homogenisation (to liquid) occurred between 301 °C and 420 °C. Some Type 1 inclusions decrepitated before total homogenisation.

T_{LM} values in Type 2 inclusions were between − 0·2 °C and − 10·1 °C and yield salinities ranging between 0·2 and 14 eq. wt.% NaCl. Type 2 inclusions have a wide range of T_{H} values (Fig. 4a, b) and homogenised to the liquid phase ($L + V \rightarrow L$) between 54 °C and 414 °C.

Type 3 inclusions were recorded in the Ardara and Main Donegal granites (Fig. 4a, b) where they occur along annealed fractures. Hydrohalite melting ($T_{M}h$) was noted in a number of Type 3 inclusions in the Ardara granite. This took place between − 29·6 °C and − 35·2 °C and was used to calculate X_{NaCl} of 0·2 to 0·36. T_{LM} values for Type 3 inclusions in the Ardara granite range from − 6·9 °C to − 13·6 °C, corresponding to salinities of 10·4 and 17·4 eq. wt.% NaCl + $CaCl_2$ (2·2–4·7 wt.% NaCl and 8·4–14·3 wt.% $CaCl_2$). Type 3 inclusions in the Main Donegal granite had lower salinities (2·7–

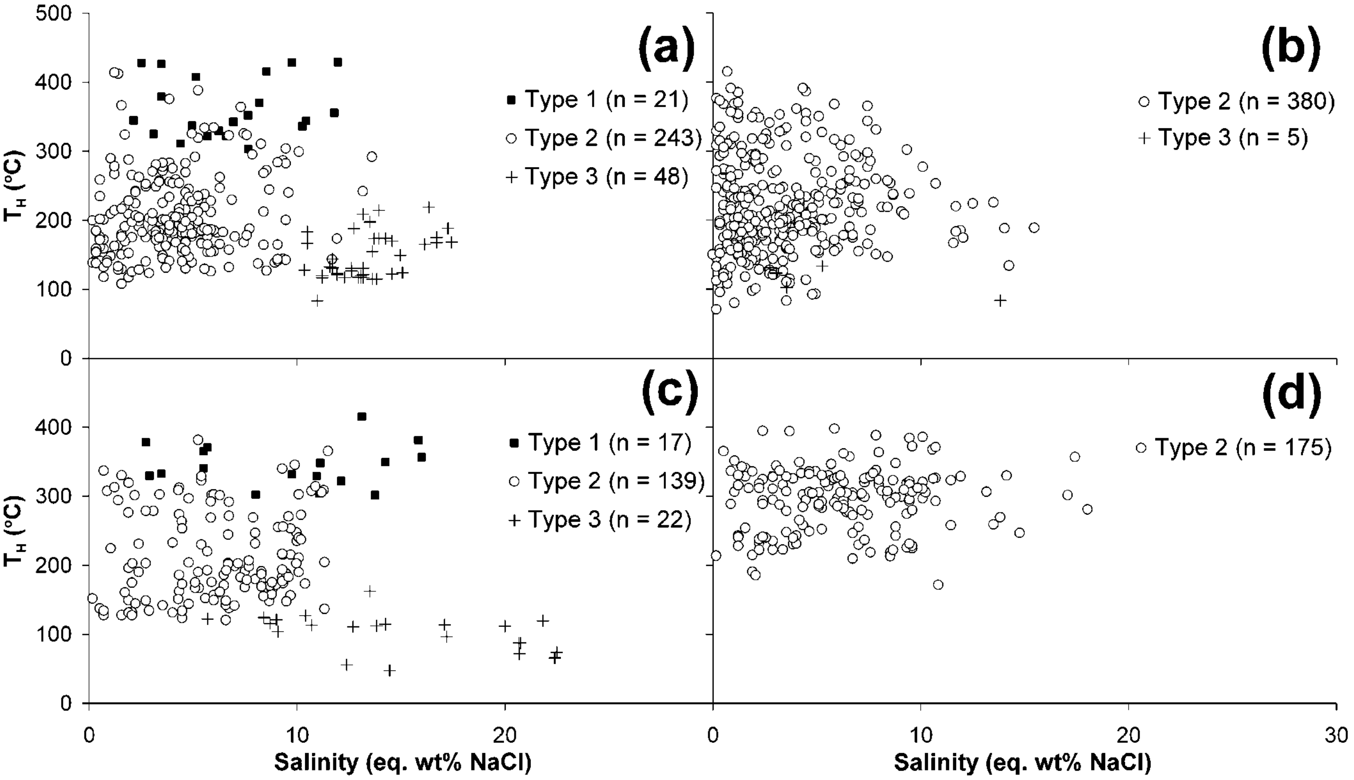

Figure 4 Bivariate plot of T_H *vs.* salinity of quartz hosted fluid inclusions. (a) Thorr and Ardara granites. (b) Main Donegal, Rosses and Trawenagh Bay granites. (c) Newry granodiorite. (d) Mourne Mountains granites.

13·8 eq. wt.% NaCl+$CaCl_2$). Type 3 inclusions homogenised to the liquid phase (L+V→L) at temperatures ranging between 84 °C and 219 °C.

3.2. Newry granodiorite

Granite quartz from the Newry granodiorite contains all three types of inclusions (Fig. 4c). Type 1 inclusions show melting of solid CO_2 close to the triple point of pure CO_2 (− 56·6 °C). Clathrate melting, in the presence of liquid CO_2, occurred between 0·7 °C and 8·4 °C, corresponding to salinities of 2·7–16 eq. wt.% NaCl. Homogenisation of the CO_2 phase (to vapour) occurred between 28·6 °C and 31·1 °C, indicating a CO_2-phase density of 0·31–0·37 g/cc. Total homogenisation (some decrepitated) to the liquid phase (L+V→L) was recorded between 301 °C and 415 °C.

In Type 2 inclusions the last ice-melting temperatures (− 0·1 °C to − 7·9 °C) correspond to a wide range of salinities (0·2–11·5 eq. wt.% NaCl). Type 2 inclusions homogenised to the liquid (L+V→L) between 120 °C and 382 °C.

Type 3 inclusions show hydrohalite melting between − 29·1 °C and − 24·5 °C, yielding X_{NaCl} values of between 0·38 and 0·65. The T_{LM} occurred between − 3·5 °C and − 20·1 °C, corresponding to salinities ranging between 5·7 and 22·5 eq. wt.% NaCl+$CaCl_2$ (4·2–18·3 wt.% NaCl and 2–13·5 wt.% $CaCl_2$). Type 3 inclusions homogenised to the liquid phase (L+V→L) between 48 °C and 211 °C.

Naturally decrepitated fluid inclusions were recorded in granite quartz from the SW end of the Newry granodiorite, indicating a significant post-emplacement increase in temperature and/or pressure. The origin of these decrepitated inclusions is considered by the present authors to be related to overheating during the emplacement of the Paleocene Slieve Gullion Igneous Complex into the Newry granodiorite at 56·6 ± 1·3 Ma (Gamble *et al.* 1999).

3.3. Mourne Mountains granite

Only Type 2 inclusions were recorded in granite quartz from the Paleocene Mourne Mountains granite (Fig. 4d). The T_{LM} occurred between − 0·1 °C and − 14·3 °C, yielding salinities of between 0·2 and 18 eq. wt.% NaCl. Type 2 inclusions homogenised to the liquid phase (L+V→L) between 171 °C and 394 °C. Some halite-bearing Type 4 inclusions have also been recorded in highly altered granite samples. Halite dissolution temperatures of between 217·6 °C and 265·7 °C were used to calculate salinities of 32·8–36·7 eq. wt.% NaCl according to the equation of Sterner *et al.* (1988). Halite dissolution in Type 4 inclusions occurs prior to total homogenisation (to the liquid phase), and was recorded between 218·7 °C and 312·2 °C.

4. Discussion

4.1. Comparison to fluid inclusion studies in other Irish granites

The fluid inclusion types recognised in this study from Donegal and Northeast Ireland broadly coincide with fluid types recognised in the granites of Connemara (Gallagher *et al.* 1992; O'Reilly *et al.* 1997a; Feely *et al.* 2006, 2007), the Kentstown granite (O'Reilly *et al.* 1997b) and the Leinster granite (Whitworth & Rankin 1989; Moran 2003). The granites of Connemara span the Caledonian orogeny and range in age from 462·5 Ma (Oughterard granite; Friedrich *et al.* 1999) to 380·1 ± 1·1 Ma (Costelloe Murvey granite; Feely *et al.* 2003). Aqueous-carbonic fluid inclusions (Type 1) have been recorded in the least-evolved granites (O'Reilly *et al.* 1997a; Feely *et al.* 2007) and, on the basis of stable isotope and microthermometric data, an origin wholly within the granite has been inferred (O'Reilly *et al.* 1997a). A later fluid influx is recorded as H_2O–NaCl ± KCl inclusions (Type 2) and has been

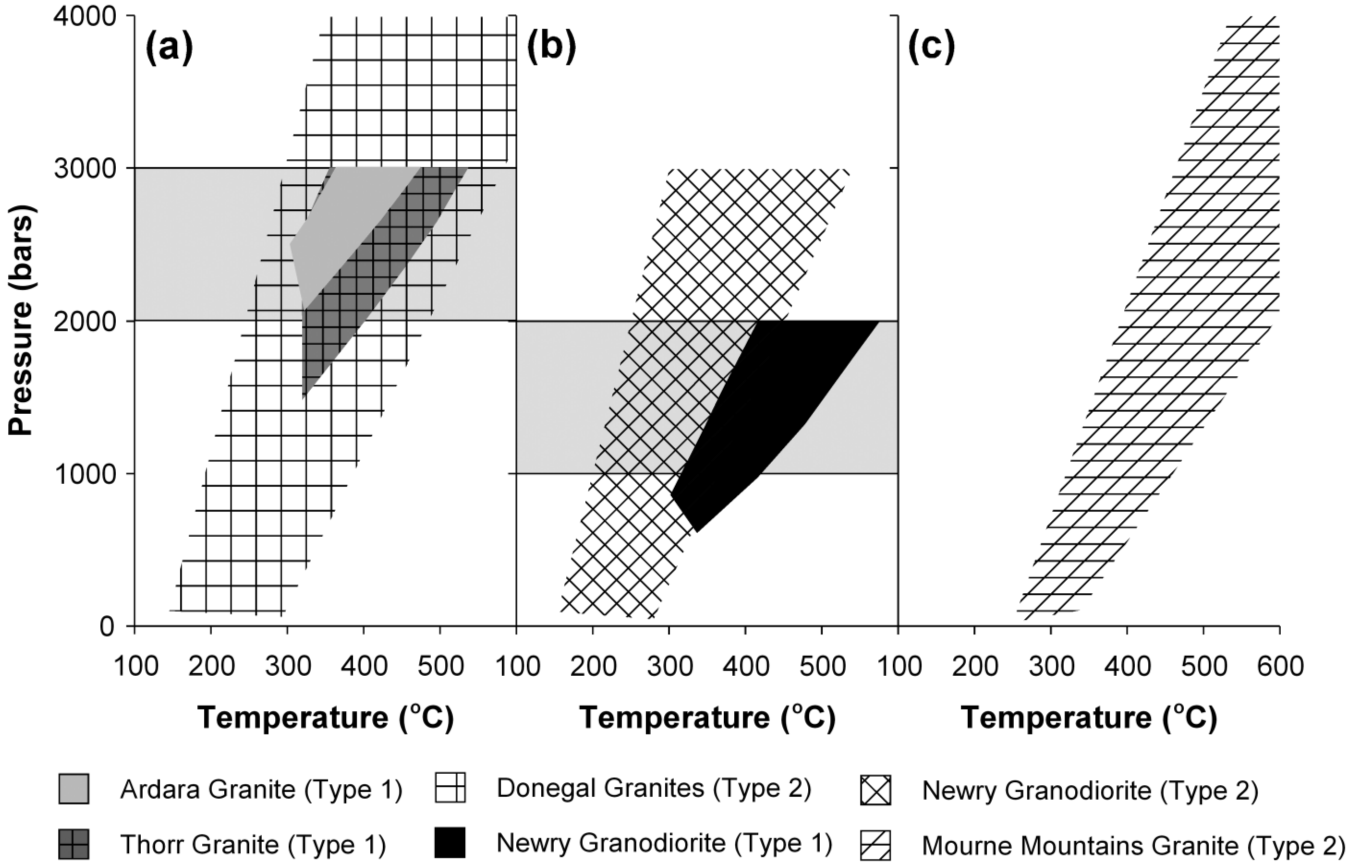

Figure 5 Pressure–Temperature space showing isochores for Type 1 and Type 2 fluid inclusions in (a) the Donegal granites, (b) the Newry granodiorite and (c) the Mourne Mountains granites. Shaded boxes show pressure constraints used to calculate trapping temperatures in the Ardara granite (2–3 kbars; Kerrick 1987) and the Newry granodiorite (1–2 kbars; Meighan *et al.* 2003b). Isochores constructed using FLUIDS (Bakker 2003).

recorded in all granites. Based on petrographic and stable isotope analyses, these inclusions were interpreted as vestiges of multiple meteoric fluid infiltrations after the crystallisation of granite quartz (O'Reilly *et al.* 1997a; Feely *et al.* 2006), consistent with geochemical analyses of white micas in the Oughterard granite (Dempster *et al.* 1994). H_2O–NaCl–$CaCl_2$ fluid inclusions (Type 3) have been recorded in the Galway granite (O'Reilly *et al.* 1997a) and Oughterard granite (Feely *et al.* 2007) and are commonly associated with base-metal bearing veins (O'Reilly *et al.* 1997a).

Late-magmatic aqueous carbonic fluids (Type 1) have been recorded in the late Caledonian Kentstown granite (O'Reilly *et al.* 1997b) but are absent from the nearby Leinster granite (Whitworth & Rankin 1989; Moran 2003). In the Kentstown and Leinster granites $H_2O+NaCl$ (Type 2) and $H_2O+NaCl+CaCl_2$ (Type 3) fluids have been recorded. Type 2 fluids are related to influxes of meteoric fluids and Type 3 fluids are attributed to an influx of basinal brines after the crystallisation of the granite (Whitworth & Rankin 1989; O'Reilly *et al.* 1997b).

4.2. P–T modelling of fluid trapping conditions

Based on fluid inclusion microthermometry, the trapping pressures (P_T) and temperatures (T_T) of Type 1 and 2 fluid inclusions in the Donegal, Newry and Mourne Mountains granites can be estimated in terms of fluid isochores (Fig. 5) and constraints on either P or T conditions determined with other methods. The PT conditions of trapping for Type 1 inclusions were constructed in the H_2O–CO_2–NaCl system using the equations of state (EOS) of Duan *et al.* (1995), and those for Type 2 inclusions in the H_2O–NaCl system using the EOS of Zhang & Frantz (1987); and isochores for both types were constructed using the software package FLUIDS (Bakker 2003).

In the Donegal granites, emplacement pressures have been estimated from the Ardara granite by Kerrick (1987). Using the garnet–plagioclase–Al_2SiO_3–quartz (GASP) geobarometer in the sillimanite zone of the Ardara aureole, this author estimated pressures of 2·5 ± 0·5 kbar for the contact metamorphism, and therefore for the emplacement pressure of the Ardara granite (and the coeval Thorr granite). For Type 1 inclusions, these P_T values correspond to T_T of 305–475 °C in the Ardara granite and 320–540 °C in the Thorr granite (Fig. 5a). In the Newry granodiorite, emplacement pressures of between 1 and 2 kbars have been estimated from amphibole geobarometry (Meighan *et al.* 2003b) and at these pressures, T_T of Type 1 fluids range from 320 °C to 575 °C (Fig. 5b). The T_T values estimated for the Type 1 inclusions are similar to the range estimated for late-magmatic aqueous carbonic fluids in the Galway granite (366–567 °C; O'Reilly *et al.* 1997a) and magmatic fluids in other granites worldwide (Sachan *et al.* 1996; Nabelek & Ternes 1997; Yang *et al.* 2004).

Type 2 inclusions have a wide range of T_H values and, therefore, isochores constructed for the Donegal, Newry and Mourne Mountains granites define a wide range of possible P_T and T_T (Fig. 5). The wide range of T_H values suggests either that fluid temperature decreased far more rapidly than did fluid pressure (isobaric cooling), or that fluid pressure decreased more rapidly than fluid temperature (decompression during uplift); or a combination of both. The only constraints on the trapping conditions of Type 3 fluids is that P_T and T_T are likely to be lower than Type 1 and Type 2 fluids.

4.3. Origin of aqueous-carbonic fluids in late Caledonian granites

Although the source of CO_2 in Type 1 inclusions remains enigmatic, a number of possible origins must be considered (Lowenstein 2001). These include (1) devolatisation reactions during regional metamorphism after granite emplacement; (2) partial melting and assimilation of crustal materials in the upper crust during emplacement; and (3) incorporation of CO_2 into magma due to the subduction-related partial melting of the lower crust or mantle.

Although aqueous-carbonic fluid inclusions associated with greenschist to amphibolite facies metamorphism have been recorded in the Dalradian metamorphic rocks of north and western Ireland (Wilkinson & Johnston 1996; Parnell *et al.* 2000), regional metamorphism predates Caledonian igneous activity (Friedrich *et al.* 1999) and is unrelated to Type 1 fluids. Stable isotope (C, O, S) data from the Galway granite show that aqueous-carbonic fluids have a wholly magmatic origin and no evidence of metamorphic fluids was recorded (Gallagher *et al.* 1992; O'Reilly *et al.* 1997a). In addition, aqueous-carbonic fluids associated with devolatisation reactions during metamorphism are characterised by high nitrogen concentrations (Huff & Nabelek 2007), while solid CO_2 melting temperatures in aqueous-carbonic inclusions from the Newry, Thorr and Ardara granites are usually within ± 1 °C of the triple point of pure CO_2, indicating the presence of little or no CH_4 or N_2.

The assimilation of greywackes, calcareous sandstones and many hydrothermally-altered rocks during granite emplacement may lead to the incorporation of CO_2 into a granitic melt (Lowenstein 2001), while skarn reactions associated with the breakdown of carbonate-rich rocks by magmatic fluids is certain to add some CO_2 to the magma (Lentz 1999). Geochemical studies have shown that a number of the granites discussed in this present paper have significant crustal components. In particular, Ghani & Atherton (2006) reported that the Main Donegal, Trawenagh Bay and Rosses granites were formed by the partial melting of old, LREE-enriched crust, while Sweetman (1987) combined wholerock geochemical data with field and petrographic evidence from the Blackstairs Unit of the Leinster granite and concluded that the source of granitic magmas was the partial melting of a Lower Palaeozoic, immature sedimentary source. However, these granites are characterised by an absence of aqueous-carbonic fluids and, although the assimilation of crustal material may have led to the incorporation of some CO_2 into the magma, it is unlikely to be the sole source of carbonic fluids.

An alternative source of carbonic fluids in granitic magma is associated with subduction-related melting of lower crustal and/or mantle material (Lowenstein 2001; Scambelluri & Philippot 2001). Touret (2001) proposed a stratified model of fluids within the continental crust, with the upper crust saturated in H_2O brines (with variable amounts of CH_4 and N_2), and the lower crust dominated by CO_2-rich fluids. In addition, the occurrence of CO_2 inclusions within mantle xenoliths supports the idea that carbonic fluids are widespread in the upper mantle (Frezzotti *et al.* 1994). CO_2 fluids may be tapped from the mantle via deep seated shear zones (Pili *et al.* 1999) and are commonly trapped in fluid inclusions in mantle-derived magmas (e.g. Santosh *et al.* 2005).

The intrusion of late Caledonian granites in Ireland and Scotland is commonly associated with major NE–SW trending transpressional faults and shear zones (e.g. Hutton 1982; Jacques & Reavy 1994) and a significant mantle component for some late Caledonian granites has been invoked by a number of authors (Stephens & Halliday 1984; Dempsey *et al.* 1990; Fowler *et al.* 2001, 2008; Ghani & Atherton 2006). Stephens & Halliday (1984) subdivided the late Caledonian granites of Scotland into two main suites based on variations in geochemistry. The Argyll Suite is characterised by relatively high Sr (>500 ppm) and Ba (>800 ppm) concentrations, and these granites are interpreted as having a significant mantle component (Stephens & Halliday 1984; Fowler *et al.* 2001, 2008). In contrast, the Cairngorm Suite has lower Sr and Ba concentrations and is interpreted as being related to the partial melting of crustal material with little or no mantle component (Stephens & Halliday 1984; Atherton & Ghani 2002). Similarly, Irish late Caledonian granites can be separated into two distinct suites based on variations in geochemistry. Suite 1 includes the Thorr, Ardara, Newry and Main Galway granites, and their geochemical signature indicates a significant mantle component and affinities to the Argyll Suite (Dempsey *et al.* 1990; Crowley 1997; Ghani & Atherton 2006). Suite 1 granites are also characterised by the presence of aqueous-carbonic fluids, consistent with a mantle-derived carbon source. Suite 2 includes the Rosses, Trawenagh Bay, Costelloe Murvey and Leinster granites and is similar to the Cairngorm Suite. The source of granitic magmas in Suite 2 granites was the partial melting of old LREE element-enriched continental crust and/or a Lower Palaeozoic immature sedimentary source (Sweetman 1987; Crowley 1997; Ghani & Atherton 2006), and the absence of aqueous-carbonic fluid inclusions in these granites reflects the absence of a mantle component in the generation of these granite magmas.

To illustrate this, Sr and Rb values from selected Irish late Caledonian granites have been plotted in Figure 6. Generally, the concentration of Sr in crust-derived melts is relatively low, because during partial melting Sr is incorporated into plagioclase within the residual phase (Dempsey *et al.* 1990). In contrast, mantle-derived melts have higher concentrations of Sr, as plagioclase is generally not stable at mantle temperatures and Sr behaves as a highly incompatible element. Suite 1 granites are characterised by high Sr values (up to 1500 ppm) and low Rb values (<200 ppm), consistent with mantle affinities. Suite 2 granites exhibit lower Sr and higher Rb values, reflecting crustal affinities. In this, Suite 1 granites are similar to the Argyll Suite of Stephens & Halliday (1984) and the Suite 2 granites resemble granites of the Cairngorm Suite; and therefore the presence or absence of aqueous-carbonic fluids in Irish late Caledonian granites reflects variation in the source of the granite magmas.

The presence of aqueous-carbonic fluids has implications for models of mineralisation associated with late Caledonian granites. Poorly developed Cu and Mo mineralisation is commonly associated with late Caledonian magmatism (Plant *et al.* 1983), and fluid inclusion studies of these deposits have shown that mineralisation is associated with magmatic CO_2-bearing fluids (Kay 1985; Gallagher *et al.* 1992; Feely *et al.* 2007; Selby *et al.* 2008). Gold mineralisation in Dalradian metamorphic rocks at Curraghinalt, Northern Ireland (Parnell *et al.* 2000) and Tyndrum, Scotland (Pattrick *et al.* 1988; Curtis *et al.* 1993) has also been linked to aqueous-carbonic magmatic fluids that may have been derived from an underlying Caledonian intrusive. Although CO_2 has only an indirect role on gold mineralisation (Lowenstern 2001), it is likely to have a significant role in magmatic fluid exsolution and evolution, and may lead to concentrations of Au, Cu and Mo into the vapour phase (Heinrich *et al.* 1999; Ulrich *et al.* 2001). Therefore, Suite 1 granites warrant attention during future mineral exploration, particularly for porphyry Cu–Mo mineralisation and for structurally-controlled Au-mineralisation distal from the intrusion.

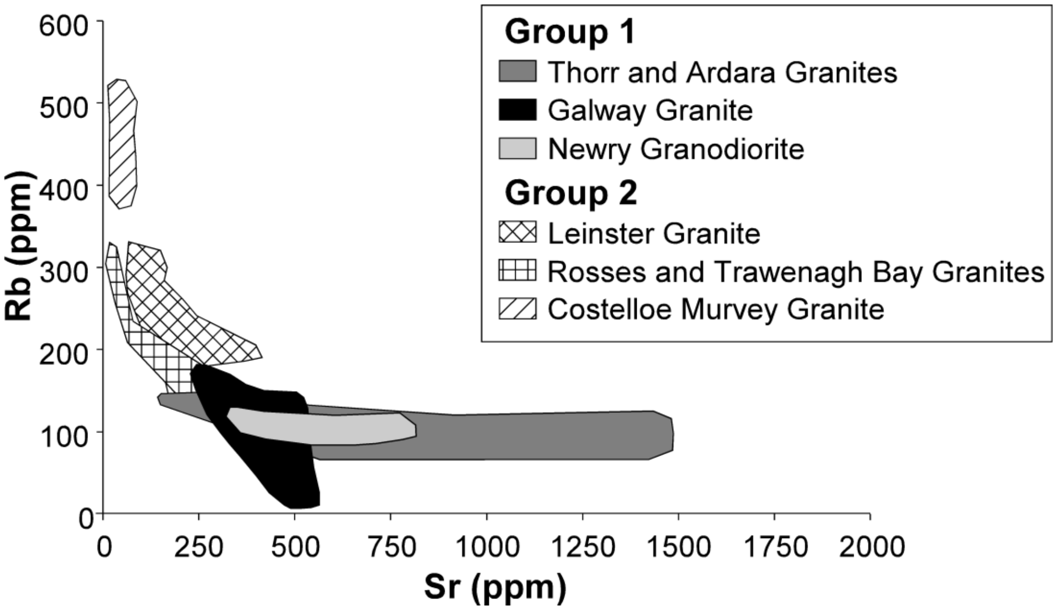

Figure 6 Comparative Rb *vs.* Sr plot for selected Irish late Caledonian granites. Data summarised from Brück & O'Connor (1977), O'Connor *et al.* (1982), Stephens & Halliday (1984), Dempsey *et al.* (1990), Crowley (1997) and Ghani & Atherton (2006).

4.4. Origin of Type 2 and Type 4 fluids

Type 2 fluid inclusions are similar to low–moderate salinity aqueous inclusions in other granites worldwide (e.g. Sachan 1996; Carruzzo *et al.* 2000; Yang *et al.* 2004). Aqueous inclusions from granite-related magmatic/hydrothermal ore deposits are often interpreted as reflecting an evolution from late-stage magmatic fluids to dominantly meteoric fluids as cooling proceeds (e.g. Audétat & Pettke 2003). Stable isotope evidence from vein and granite quartz in the Galway granite (Gallagher *et al.* 1992; O'Reilly *et al.* 1997a) and the Oughterard granite (Feely *et al.* 2006) indicate that Type 2 fluids in Irish granites are dominantly meteoric in origin. O'Reilly *et al.* (1997a) considered that H_2O–NaCl fluids in granite quartz from the Galway granite were associated with a hydrothermal convection cell which developed around the Galway granite, and this fluid influx has been linked to the resetting of hornblende K–Ar ages in the surrounding Connemara metasediments, up to 16 km from the nearest contact of the granite (Jappy *et al.* 2001). Alternatively, $H_2O + NaCl \pm KCl$ fluid influxes recorded in these granites and the surrounding country rocks may in part be related to regional scale influxes of surface-derived fluid post-granite emplacement. Analyses of the hydraulic conductivity of granitic rocks have shown that they can be highly conductive above the brittle–ductile transition in the upper crust (typically 12–14 km; Stober & Bucher 2007), and evidence for an influx of surface-derived fluids similar to Type 2 fluids has also been reported from late-stage quartz in the Curraghinalt gold prospect, Northern Ireland (Parnell *et al.* 2000) and gold mineralisation at Croagh Patrick, western Ireland (Wilkinson & Johnston 1996). It is therefore plausible that Type 2 fluids are associated with a regional scale influx of surface-derived fluids at the end of the Caledonian orogen, similar to tectonically-controlled infiltrations of meteoric fluids during uplift in other post-orogenic terraines (Jenkin *et al.* 1994; Möller *et al.* 1997).

Stable isotope analysis from the Mourne Mountains granite shows that influxes of meteoric waters were restricted to the margins of the pluton and internal contacts (McCormick *et al.* 1993). High-salinity Type 4 inclusions in the Mourne Mountains granites are associated with these locations, and may reflect the local influx of surface-derived fluids which circulated through overlying evaporitic deposits. The non-pervasive nature of meteoric fluid influxes is consistent with the tectonic setting of the Mourne Mountains granite, which was emplaced at relatively shallow crustal depths during continental rifting associated with the opening of the North Atlantic. In contrast to late Caledonian granites, meteoric fluid influxes in the Mourne Mountains granite are solely related to convection cells activated by the thermal anomaly associated with granite emplacement and the granite has been unaffected by regional-scale fluid influxes.

4.5. Origin of Type 3 fluids

Type 3 inclusions are characterised by low homogenisation temperatures, moderate to high salinities and the presence of Ca^{2+} ions in solution. The wide salinity range of Type 3 inclusions in the Ardara and Newry granites suggests that they represent the mixing of two or more fluids. In particular, compositional data from these granites reveal variations in fluid Na:Ca ratios (Fig. 7). The Ardara granite data indicate that the end-member fluids are a low-salinity NaCl-dominated fluid and a high-salinity $CaCl_2$-rich fluid. However, the Newry granodiorite data possess evidence of fluid mixing between a high-salinity NaCl-rich end-member with a $CaCl_2$-rich end-member. Similar trends have been recorded from the Kentstown, Oughterard and Galway granites (O'Reilly *et al.* 1997a, b; Feely *et al.* 2006; see Fig. 7). These compositional variations between granite plutons are not consistent with horizontal flow systems through the Irish Crust, which tend to show little or no lateral variations in fluid chemistry (Shelton *et al.* 1992). In addition, the wide range of homogenisation temperatures (from 112 ± 38 °C in the Newry granodiorite to 170 ± 30 °C in the Leinster granite) and their absence in the Thorr, Rosses and Trawenagh Bay granites are inconsistent with a regional-scale horizontal fluid flux. However, such variations are consistent with the deep penetration of surface-derived fluids into the crystalline basement, when lateral variations can be recorded on the kilometre scale (Everett *et al.* 1999a) and fluid salinities and compositions are controlled by interactions with basement lithologies.

The infiltration of moderate- to high-salinity brines into crystalline basement rocks is well documented (Möller *et al.*

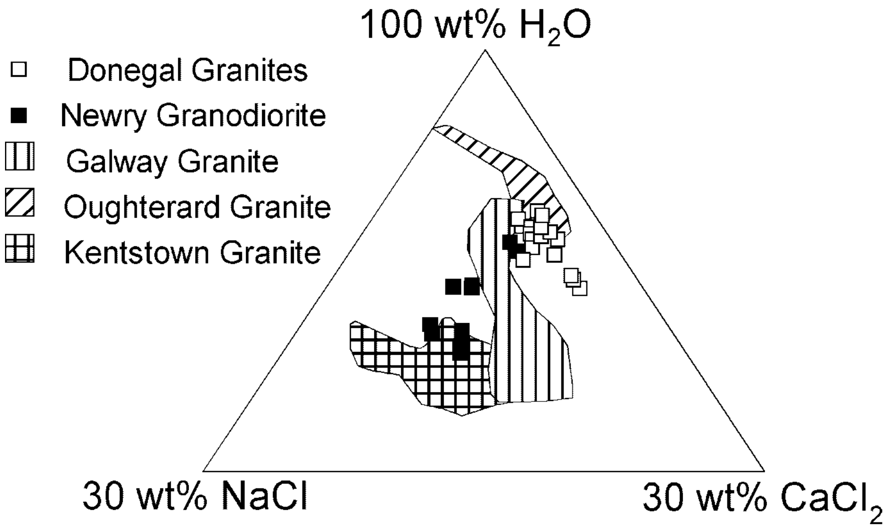

Figure 7 Composition of $H_2O+NaCl+CaCl_2$ fluids from the Ardara granite and Newry granodiorite. Also included are fields defined from the Oughterard granite (Feely *et al.* 2006) Galway granite (O'Reilly *et al.* 1997a) and Kentstown granite (O'Reilly *et al.* 1997b). Salinities calculated from combined $T_{M}h$ and T_{LM} data using programs of Chi & Ni (2007).

1997; Yardley *et al.* 2000; Gleeson *et al.* 2003; Anderson *et al.* 2004). The downward migration of basinal fluids into basement rocks is facilitated by the fracturing of brittle dry crust, particularly if the basin fluids are overpressured (Yardley *et al.* 2000). Anderson *et al.* (2004) reported on warm saline fluids associated with base-metal mineralisation in Dalradian rocks in Scotland, and concluded that fracturing associated with crustal extension would have led to the rupturing of the overlying sedimentary rocks and the downward migration of basinal fluids, and a similar mechanism for the infiltration of $NaCl–CaCl_2$-bearing fluids into Irish granites is envisaged in the present paper.

The deep penetration of $NaCl–CaCl_2$-rich brines similar to Type 3 fluids has also been recorded in the Dalradian of Northern Ireland (Wilkinson *et al.* 1999; Parnell *et al.* 2000) and lower Palaeozoic basement rocks in the Irish Midlands (Everett *et al.* 1999a). These fluids were responsible for transporting base metals into the shallow ore-forming environment (Everett *et al.* 1999a), and therefore age data from base-metal deposits in the overlying sedimentary basins may provide information of the timing of Type 3 fluid influxes in Irish granites. The timing of Zn–Pb mineralisation in the Irish Midlands remains controversial (Wilkinson 2003). Symons *et al.* (2002) proposed, on palaeomagnetic grounds, a late Arundian to early Asbian age (333 ± 4 Ma) for mineralisation at Navan. However, this age may be subject to significant error (Wilkinson 2003) and, based on the relationship between mineralisation and faulting, a Chadian age for mineralisation is preferred by most workers (Blakeman *et al.* 2002; Wilkinson 2003). However, a Lower Carboniferous age for mineralisation is not in doubt, and a Chadian age is consistent with the penetration of basinal fluids into the basement during a period of crustal extension (Russell 1978; Samson & Russell 1987; Everett *et al.* 1999a, b).

In addition to a Lower Carboniferous mineralisation event, a Permo-Triassic age has been reported for base-metal mineralisation in Northern Ireland (Pannalal *et al.* 2006). These authors reported on chemical remanent magnetisation of hematite, magnetite and pyrrhotite in Lower Carboniferous carbonates in Northern Ireland, which revealed two regional scale fluid influxes, during Lower Carboniferous (326 ± 4 Ma), and Triassic (239 ± 7 Ma) times. A Triassic age for Type 3 fluid influxes is consistent with a maximum age for Type 3 fluids in the Galway granites, where base metal veins crosscut a dolerite dyke with a clinopyroxene $^{40}Ar/^{39}Ar$ age of 231 ± 4 Ma (O'Connor *et al.* 1993). Similar Permo-Triassic hydrothermal fluid influxes have been recorded throughout Europe (e.g. Halliday & Mitchell 1984; Möller *et al.* 1997; Gleeson *et al.* 2000) associated with crustal extension during the opening of the North Atlantic. Therefore, Type 3 in granite quartz may be related to a number of periods of extension of the Irish crust, facilitating the penetration of surface derived fluids into the crystalline basement.

5. Conclusions

This study demonstrates that the crystalline basement rocks of Ireland have been affected by a series of fluid influxes, associated with certain tectonic settings. Three fluids have affected the Donegal, Newry and Mourne Mountains granites, and these fluids are broadly similar to fluid types recorded in other studies of Irish granites. A H_2O+CO_2+NaCl (Type 1) fluid has been recorded in a number of late Caledonian granites (i.e. Thorr granite, Ardara granite, Newry granodiorite, Galway granite and Kentstown granite). Geochemical analyses indicate that these granites have a significant mantle component, and this is interpreted as the most likely source of carbonic fluids. The absence of aqueous-carbonic fluid inclusions in other late Caledonian granites reflects the lower mantle component of these granite magmas.

$H_2O+NaCl \pm KCl$ (Type 2) fluids have been recorded in all samples, regardless of age or tectonic setting. These fluids are compositionally similar to inclusions in the Galway granite (O'Reilly *et al.* 1997a), Leinster granite (Moran 2003) and Kentstown granite (O'Reilly *et al.* 1997b), where they are interpreted as being related to meteoric fluid influxes shortly after their intrusion, and they may be related to the downward migration of meteoric fluids along major structural conduits after granite emplacement. Finally, $H_2O+NaCl+CaCl_2$ (Type 3) fluids occur in granite quartz from the Oughterard, Galway, Ardara, Newry, Kentstown and Leinster granites. These fluids represent the deep penetration of brines during a period of crustal extension, possibly during the Carboniferous or the Triassic.

6. Acknowledgements

JC acknowledges funding provided by a National University of Ireland, Galway Postgraduate Fellowship. Siobhan Power and Aoife Braiden are thanked for their assistance in the field. D. Alderton and an anonymous reviewer are thanked for their comments.

7. References

Anderson, R., Graham, C. M., Boyce, A. J. & Fallick, A. E. 2004. Metamorphic and basin fluids in quartz–carbonate6sulphide veins in the SW Scottish Highlands; a stable isotope and fluid inclusion study. *Geofluids* **4**, 169–85.

Atherton, M. P. & Ghani, A. A. 2002. Slab breakoff: A model for Caledonian, Late Granite syn-collisional magmatism in the orthotectonic (metamorphic) zone of Scotland and Donegal, Ireland. *Lithos* **62**, 65–85.

Audétat, A. & Pettke, T. 2003. The magmatic–hydrothermal evolution of two barren granites: a melt and fluid inclusion study of the Rito del Medio and Canada Pinabete plutons in northern New Mexico (USA). *Geochimica et Cosmochimica Acta* **67**, 97–121.

Bakker, R. J. 1997. Clathrates: computer programs to calculate fluid inclusion V–X properties using clathrate melting temperatures. *Computers and Geosciences* **23**, 1–18.

Bakker, R. J. 2003. Package FLUIDs 1. Computer programs for analysis of fluid inclusion data and for modelling bulk fluid properties. *Chemical Geology* **194**, 3–23.

Blakeman, R. J., Ashton, J. H., Boyce, A. J., Fallick, A. E. & Russell, M. J. 2002. Timing of Interplay between Hydrothermal and Surface Fluids in the Navan Zn+Pb Orebody, Ireland: Evidence from Metal Distribution Trends, Mineral Textures, and δ^{34}S Analyses. *Economic Geology* **97**, 73–91.

Bodnar, R. J. 1993. Revised equation and table for determining the freezing point depression of H_2O–NaCl solutions. *Geochimica et Cosmochimica Acta* **57**, 683–84.

Bruck, P. M. & O'Connor, P. J. 1977. The Leinster Batholith; geology and geochemistry of the northern units. *Bulletin of the Geological Survey of Ireland* **2**, 107–41.

Carruzzo, S., Kontak, D. J. & Clarke, D. B. 2000. Granite-hosted mineral deposits of the New Ross area, South Mountain Batholith, Nova Scotia, Canada; P, T, and X constraints of fluids using fluid inclusion thermometry and decrepitate analysis. *Transactions of the Royal Society of Edinburgh: Earth Sciences* **91** (1–2), 303–19.

Chi, G. & Ni, P. 2007. Equations for calculation of NaCl/(NaCl+$CaCl_2$) ratios and salinities from hydrohalite-melting and ice-melting temperatures in the H_2O–NaCl–$CaCl_2$ system. *Acta Petrologica Sinica* **22**, 33–37.

Condon, D. J., Bowring, S. A., Pitcher, W. S. & Hutton, D. W. H. 2004. Rates and tempo of granitic magmatism; a U–Pb geochronological investigation of the Donegal Batholith (Ireland). *Geological Society of America Abstracts with Programs* **36**, 406. Boulder, Colorado and Lawrence, Kansas: The Geological Society of America and University of Kansas Press.

Crowley, Q. 1997. *The Geology and Geochemistry of the Galway Granite in the Inveran Sector, Western Ireland*. Unpublished PhD Thesis, University College Galway, Ireland.

Curtis, S. F., Pattrick, R. A. D., Jenkin, G. R. T., Fallick, A. E., Boyce, A. J. & Treagus, J. E. 1993. Fluid inclusion and stable isotope study of fault-related mineralization in Tyndrum area, Scotland. *Transactions of the Institution of Mining and Metallurgy. Section B: Applied Earth Science* **102**, 39–47.

Dempsey, C. S., Halliday, A. N. & Meighan, I. B. 1990. Combined Sm–Nd and Rb–Sr isotope systematics in the Donegal granitoids and their petrogenetic implications. *Geological Magazine* **127**, 75–80.

Dempster, T. J., Tanner, P. W. G. & Ainsworth, P. 1994. Chemical zoning of white micas: A record of fluid infiltration in the Oughterard granite, western Ireland. *American Mineralogist* **79**, 536–44.

Dewey, J. F. & Mange, M. 1999. Petrography of Ordovician and Silurian sediments in the western Irish Caledonides: traces of a short-lived Ordovician continent-arc collision orogeny and the evolution of the Laurentian Appalachian–Caledonian margin. *In* MacNiocaill, C. & Ryan, P. D. (eds) *Continental Tectonics. Geological Society, London, Special Publication* **164**, 55–107.

Duan, Z., Møller, N. & Weare, J. H. 1995. Equation of state for the NaCl–H_2O–CO_2 system: prediction of phase equilibria and volumetric properties. *Geochimica et Cosmochimica Acta* **59**, 2869–82.

Everett, C. E., Wilkinson, J. J. & Rye, D. M. 1999a. Fracture-controlled fluid flow in the Lower Palaeozoic basement rocks of Ireland: implications for the genesis of Irish-type Zn–Pb deposits. *Geological Society Special Publication* **155**, 247–76. Bath, UK: The Geological Society Publishing House.

Everett, C. E., Wilkinson, J. J., Boyce, A. J., Ellam, R. M., Fallick, A. E., Gleeson, S. A. & Blakeman, R. 1999b. The genesis of Irish-type Zn–Pb deposits: characterisation and origin of the principal ore fluid. *In* Stanley, C. J. (ed.) *Mineral deposits: processes to processing. Proceedings of the Joint SGA–IAGOD Symposium, London* **2**, 845–48. Rotterdam: AA Balkema.

Feely, M., Coleman, D., Baxter, S. & Miller, B. 2003. U–Pb zircon geochronology of the Galway Granite, Connemara, Ireland: implications for the timing of late Caledonian tectonic and magmatic events and for correlations with Acadian plutonism in New England. *Atlantic Geology* **39**, 175–84.

Feely, M., Conliffe, J., Faure, K. & Power, S. E. 2006. Fluid inclusion trails in granite quartz: evidence for aqueous fluid infiltration in the Oughterard Granite, Eastern Connemara. *Irish Journal of Earth Science* **24**, 1–11.

Feely, M., Selby, D., Conliffe, J. & Judge, M. 2007. Re/Os geochronology and fluid inclusion microthermometry of molybdenite mineralisation in the late Caledonian Omey Granite, western Ireland. *Transactions of the Institution of Mining and Metallurgy. Section B: Applied Earth Science* **116**, 143–49.

Fowler, M. B., Henney, P. J., Darbyshire, D. P. F. & Greenwood, P. B. 2001. Petrogenesis of high Ba–Sr granites: the Rogart pluton, Sutherland. *Journal of the Geological Society, London* **158**, 521–34.

Fowler, M. B., Kocks, H., Darbyshire, D. P. F. & Greenwood, P. B. 2008. Petrogenesis of high Ba–Sr plutons from the Northern Highlands Terrane of the British Caledonian Province. *Lithos* **105**, 129–48.

Frezzotti, M. L., Di Vincenzo, G., Ghezzo, C. & Burke, E. A. J. 1994. Evidence of magmatic CO_2-rich fluids in peraluminous graphite-bearing leucogranites from Deep Freeze Range (northern Victoria Land, Antarctica). *Contributions to Mineralogy and Petrology* **117**, 111–23.

Friedrich, A. M., Bowring, S. A., Martin, M. W. & Hodges, K. V. 1999. Short-lived continental magmatic arc at Connemara, western Irish Caledonides: Implications for the age of the Grampian orogeny. *Geology* **27**, 27–30.

Gallagher, V., Feely, M., Hogelsberger, H., Jenkin, G. R. T. & Fallick, A. E. 1992. Geological, fluid inclusion and stable isotope studies of Mo mineralisation, Galway Granite, Ireland. *Mineral Deposita* **27**, 314–25.

Gamble, J. A., Wysoczanski, R. J. & Meighan, I. G. 1999. Constraints on the age of the British Tertiary Volcanic Province from ion microprobe U–Pb (SHRIMP) ages for acid igneous rocks from NE Ireland. *Journal of the Geological Society, London* **156**, 291–99.

Ghani, A. A. & Atherton, M. P. 2006. The chemical character of the Late Caledonian Donegal Granites, Ireland, with comments on their genesis. *Transactions of the Royal Society of Edinburgh: Earth Sciences* **97**, 437–54.

Gleeson, S. A., Wilkinson, J. J., Shaw, H. F. & Herrington, R. J. 2000. Post-magmatic hydrothermal circulation and the origin of base metal mineralization, Cornwall, UK. *Journal of the Geological Society, London* **157**, 589–600.

Gleeson, S. A., Yardley, B. W. D., Munz, I. A. & Boyce, A. J. 2003. Infiltration of basinal fluids into high-grade basement, South Norway; sources and behaviour of waters and brines. *Geofluids* **3**, 33–48.

Goldstein, R. H. 2003. Petrographic analysis of fluid inclusions. *In* Samson, I. M., Anderson, A. & Marshall, D. (eds) *Fluid Inclusions: Analysis and Interpretation. Mineralogical Association of Canada Short Course Series* **32**. Vancouver: Mineralogical Association of Canada.

Halliday, A. N., Aftalion, M. & Leake, B. E. 1980. A revised age for the Donegal granites. *Nature* **284**, 542–44.

Halliday, A. N. & Mitchell, J. G. 1984. K–Ar ages of clay-size concentrates from the mineralization of the Pedroches Batholith, Spain, and evidence for Mesozoic hydrothermal activity associated with the break up of Pangaea. *Earth and Planetary Science Letters* **68**, 229–39.

Heinrich, C. A., Guenther, D., Audetat, A., Ulrich, T. & Frischknecht, R. 1999. Metal fractionation between magmatic brine and vapor, determined by microanalysis of fluid inclusions. *Geology* **27**, 755–58.

Huff, T. A. & Nabelek, P. I. 2007. Production of carbonic fluids during metamorphism of graphitic pelites in a collisional orogen – An assessment from fluid inclusions. *Geochemica et Cosmochimica Acta* **71**, 4997–5015.

Hutton, D. H. W. 1982. A tectonic model for the emplacement of the Main Donegal Granite, NW Ireland. *Journal of the Geological Society, London* **1982**, 615–31.

Jacques, J. M. & Reavy, R. J. 1994. Caledonian plutonism and major lineaments in the SW Scottish Highlands. *Journal of the Geological Society, London* **151**, 955–69.

Jappy, T. G., Leake, B. E. & Fallick, A. E. 2001. Relationships between hornblende K–Ar ages, chemical composition and hydrogen isotopes, Connemara, western Ireland: evidence for a massive extinct hydrothermal system. *Journal of the Geological Society, London* **158**, 843–54.

Jenkin, G. R. T., Craw, D. & Fallick, A. E. 1994. Stable isotopic and fluid inclusion evidence for meteoric fluid penetration into an active mountain belt; Alpine Schist, New Zealand. *Journal of Metamorphic Geology* **12**, 429–44.

Kay, E. A. 1985. *Hydrothermal Alteration and Mineralization of the Lagalochan Au–Cu–Mo Prospect, Western Scotland.* Unpublished PhD Thesis. University of London.

Kerrick, D. M. 1987. Fibrolite in contact aureoles of Donegal, Ireland. *American Mineralogist* **72**, 240–54.

Lentz, D. R. 1999. Carbonatite genesis; a reexamination of the role of intrusion-related pneumatolytic skarn processes in limestone melting. *Geology* **27**, 335–38.

Lowenstern, J. B. 2001. Carbon dioxide in magmas and implications for hydrothermal systems. *Mineralium Deposita* **V36**, 490–502.

McCormick, A. G., Gibson, D., Fallick, A. E., Harmon, R. S. & Meighan, I. G. 1993. Oxygen and hydrogen isotope geochemistry of the Mourne Mountains Tertiary granites, Northern Ireland. *Journal of Petrology* **34**, 1177–202.

Meighan, I. G., Gibson, D. & Hood, D. N. 1984. Some aspects of Tertiary acid magmatism in NE Ireland. *Mineralogical Magazine* **48**, 351–63.

Meighan, I. G., Fallick, A. E. & McCormick, A. G. 1992. Anorogenic granite magma genesis: new isotopic data for the southern sector of the British Tertiary Igneous Province. *Transactions of the Royal Society of Edinburgh: Earth Sciences* **83**, 227–33.

Meighan, I. G., Hamilton, M. A., Gamble, J. A., Ellam, R. M. & Cooper, M. R. 2003a. The Caledonian Newry complex, NE Ireland: new U–Pb ages, a subsurface extension and magmatic epidote. *In GSA Program with Abstracts (Northeastern Section — 38th Annual Meeting, March 2003)* **35**(3), 79–80.

Meighan, I. G., Cooper, M. R. & Tindle, A. G. 2003b. Magmatic-like epidote in the Newry Igneous Complex. *In* Sanders, I. (ed.) *Abstracts of the 45th Irish Geological Research Meeting. Irish Journal of Earth Sciences* **21**, 156.

Meighan, I. G. & Neeson, J. C. 1979. The Newry igneous complex, County Down. *In* Harris, A. L., Holland, C. H. & Leake, B. E. (eds) *The Caledonides of the British Isles – Reviewed. Geological Society, London, Special Publications* **8**, 717–22. Bath, UK: The Geological Society Publishing House.

Möller, N., Behr, H. J., Borchardt, R., Brauer, K., Drescher, J., Erzinger, J., Faber, E., Hansen, B. T., Horn, E. E., Huenges, E., Kampf, H., Kessels, W., Kirsten, T., Landwehr, D., Lodenmann, M., Machon, L., Pekdeger, A., Pielow, H. U., Reutel, C., Simon, K., Walther, J,. Weinlich, F. H., Zimmer, M., Weise, S. M., Althaus, E. & Bach, W. 1997. Paleofluids and Recent fluids in the upper continental crust: results from the German Continental Deep Drilling Program (KTB). *Journal of Geophysical Research* **102**, 18233–54.

Moran, R. 2003. *Fluid inclusion studies of the Leinster Granite, southeast Ireland, and its Quartz veins.* Unpublished MSc Thesis. National University of Ireland, Galway.

Nabelek, P. I. & Ternes, K. 1997. Fluid inclusions in the Harney Peak Granite, Black Hills, South Dakota, USA: Implications for solubility and evolution of magmatic volatiles and crystallization of leucogranite magmas. *Geochimica et Cosmochimica Acta* **61**, 1447–65.

O'Connor, P. J., Max, M. D., Roddick, J. C., Long, C. B., Kennan, P. S. & Halliday, A. N. 1982. Rb–Sr isochron study of the Thorr and Main Donegal granites, Ireland. *Geological Journal* **17**, 279–95.

O'Connor, P. J., Long, C. B. & Evans, J. A. 1987. Rb–Sr wholerock isochron studies of the Barnesmore and Fanad plutons, Donegal, Ireland. *Geological Journal* **22**, 11–23.

O'Connor, P. J., Hogelsberger, H., Feely, M. & Rex, D. C. 1993. Fluid inclusion studies, rare-earth element chemistry and age of hydrothermal fluorite mineralisation in western Ireland – a link with continental rifting? *Transactions of the Institution of Mining & Metallurgy, Section B (Applied Earth Science)* **102**, 141–48.

O'Reilly, C., Fallick, A. E., Jenkin, G. R. T., Feely, M. & Alderton, D. H. M. 1997a. A fluid inclusion and stable isotope study of 200 Ma of fluid evolution in the Galway Granite, Connemara, Ireland. *Contributions to Mineralogy and Petrology* **129** 120–42.

O'Reilly, C., Feely, M., Holdstock, M. P. & O'Keefe, W. G. 1997b. Fluid inclusion study of the unexposed Kentstown Granite, Co. Meath, Ireland. *Transactions of the Institution of Mining & Metallurgy, Section B (Applied Earth Science)* **106**, 31–37.

Pannalal, S. J., Symons, D. T. A., Sangster, D. F. & Stanley, G. A. 2006. Brigantian and Middle Triassic remagnetizations in Lower Carboniferous carbonates, Northern Ireland: Role of diagenesis and fluid flow. *Journal of Geochemical Exploration* **89**, 309–13.

Parnell, J., Earls, G., Wilkinson, J. J., Hutton, D. H. W., Boyce, A. J., Fallick, A. E., Ellam, R. M., Gleeson, S. A., Moles, N. R., Legg, I. & Carey, P. F. 2000. Regional Fluid Flow and Gold Mineralization in the Dalradian of the Sperrin Mountains, Northern Ireland. *Economic Geology* **95**, 1389–416.

Pattrick, R. A. D., Boyce, A. & McIntyre, R. M. 1988. Gold-silver vein mineralization at Tyndrum, Scotland. *Mineralogy and Petrology* **38**, 61–76.

Pili, E., Sheppard, S. M. F. & Lardeaux, J. M. 1999. Fluid–Rock Interaction in the Granulites of Madagascar and Lithospheric-Scale Transfer of Fluids. *Gondwana Research* **2** (3), 341–50.

Pitcher, W. S. & Berger, A. R. 1972. *The Geology of Donegal; a study of granite emplacement and unroofing*. New York: Wiley-Interscience.

Plant, J. A., Simpson, P. R., Green, P. M., Watson, J. V. & Fowler, M. B. 1983. Metalliferous and mineralized Caledonian granites in relation to regional metamorphism and fracture systems in Northern Scotland. *Transactions of the Institution of Mining & Metallurgy, Section B (Applied Earth Science)* **92**, 33–42.

Rankin, A. H. & Alderton, D. H. M. 1985. Fluids in granites from Southwest England. *In High heat production (HHP) granites, hydrothermal circulation and ore genesis*, 287–99. London: Institute of Mining and Metallurgy.

Reid, H. H. 1961. Aspects of Caledonian magmatism in Britain. *Proceedings of the Liverpool and Manchester Geological Society* **2**, 653–83.

Russell, M. J. 1978. Downward-excavating hydrothermal cells and Irish-type ore deposits; importance of an underlying thick Caledonian prism. *Transactions of the Institution of Mining and Metallurgy. Section B (Applied Earth Science)* **87**, 168–70.

Sachan, H. K. 1996. Cooling history of subduction related granite from the Indus Suture Zone, Ladakh, India: evidence from fluid inclusions. *Lithos* **38**, 81–92.

Samson, I. M. & Russell, M. J. 1987. Genesis of Silvermines zinc–lead–barite deposit, Ireland: Fluid inclusion and stable isotope evidence. *Economic Geology* **82**, 371–94.

Santosh, M., Tanaka, K. & Yoshimura, Y. 2005. Carbonic fluid inclusions in ultrahigh-temperature granitoids from southern India. *Comptes Rendus Geosciences* **337**, 327–35.

Scambelluri, M. & Philippot, P. 2001. Deep fluids in subduction zones. *Lithos* **55** 213–27.

Selby, D., Conliffe, J., Crowley, Q. G. & Feely, M. 2008. Geochronology (Re–Os, U–Pb) & fluid inclusion studies of molybdenite mineralisation associated with the Shap, Skiddaw & Weardale Granites, UK. *Transactions of the Institution of Mining and Metallurgy. Section B (Applied Earth Science)* **117**, 11–28.

Shelton, K. L., Bauer, R. M. & Gregg, J. M. 1992. Fluid-inclusion studies of regionally extensive epigenetic dolomites, Bonneterre Dolomite (Cambrian), southeast Missouri: Evidence of multiple fluids during dolomitization and lead-zinc mineralization. *Geological Society of America, Bulletin* **104**, 675–83.

Shepherd, T. J., Rankin, A. H. & Alderton, D. H. M. 1985. *A practical guide to fluid inclusions*. London: Blackie.

Stephens, W. E. & Halliday, A. N. 1984. Geochemical contrasts between late Caledonian granitoid plutons of northern, central and southern Scotland. *Transactions of the Royal Society of Edinburgh: Earth Sciences* **75** (2), 259–73.

Sterner, S. M., Hall, D. L. & Bodnar, R. J. 1988. Synthetic fluid inclusions. V. Solubility relations in the system NaCl–KCl–H_2O under vapor-saturated conditions. *Geochimica et Cosmochimica Acta* **52**(5), 989–1005.

Stevenson, C. T. E., Owens, W. H., Hutton, D. H. W., Hood, D. N., Meighan, I. G., White, W. C. & Patterson, E. M. 2007. Laccolithic, as opposed to cauldron subsidence, emplacement of the Eastern Mourne pluton, N. Ireland: evidence from anisotropy of magnetic susceptibility. *Journal of the Geological Society, London* **164**, 99–110.

Stober, I. & Bucher, K. 2007. Hydraulic properties of the crystalline basement. *Hydrogeology Journal* **15**, 213–24.

Sweetman, T. M. 1987. The geochemistry of the Blackstairs Unit of the Leinster Granite, Ireland. *Journal of the Geological Society, London* **144**, 971–84.

Symons, D. T. A., Smethurst, M. T. & Ashton, J. H. 2002. Paleomagnetism of the Navan Zn–Pb Deposit, Ireland. *Economic Geology* **97**, 997–1012.

Touret, J. L. R. 2001. Fluids in metamorphic rocks. *Lithos* **55**, 1–25.

Ulrich, T., Gunther, D. & Heinrich, C. A. 2001. The evolution of a porphyry Cu–Au deposit, Based on LA-ICP-MS analysis of fluid inclusions: Bajo de la Alumbrera, Argentina. *Economic Geology* **96**, 1743–74.

Whitworth, M. P. & Rankin, A. H. 1989. Evolution of fluid phases associated with lithium pegmatites from SE Ireland. *Mineralogical Magazine* **53**, 271–84.

Wilkinson, J. J. & Johnston, J. D. 1996. Pressure fluctuations, phase separation, and gold precipitation during seismic fracture propagation. *Geology* **24**, 395–98.

Wilkinson, J. J., Boyce, A. J., Earls, G. & Fallick, A. E. 1999. Gold remobilization by low-temperature brines; evidence from the Curraghinalt gold deposit, Northern Ireland. *Economic Geology* **94**, 289–96.

Wilkinson, J. J. 2003. On diagenesis, dolomitisation and mineralisation in the Irish Zn–Pb orefield. *Mineralium Deposita* **38**, 968–83.

Yang, X. M., Lentz, D. R., Chi, G. & Kyser, T. K. 2004. Fluid-mineral reaction in the Lake George granodiorite, New Brunswick, Canada: Implications for Au–W–Mo–Sb mineralization. *Canadian Mineralogist* **42**, 1443–64.

Yardley, B. W. D., Gleeson, S. A., Bruce, S. & Banks, D. A. 2000. Origin of retrograde fluids in metamorphic rocks. *Journal of Geochemical Exploration* **69–70**, 281–85.

Zhang, Y.-G. & Frantz, J. D. 1987. Determination of the homogenization temperatures and densities of supercritical fluids in the system NaCl–KCl–$CaCl_2$–H_2O using synthetic fluid inclusions. *Chemical Geology* **64**, 335–50.

MS received 12 April 2009. Accepted for publication 19 March 2010.