

Relationships between hornblende K–Ar ages, chemical composition and hydrogen isotopes, Connemara, western Ireland: evidence for a massive extinct hydrothermal system

T. G. JAPPY^{1,2}, B. E. LEAKE^{1,3} & A. E. FALLICK⁴

¹Department of Geology and Applied Geology, University of Glasgow, Glasgow G12 8QQ, UK

²M-I Drilling Fluids UK Limited, Research and Technology Centre, 1 Abbotswell Road, West Tullos, Aberdeen AB12 3AD, UK

³Department of Earth Sciences, Cardiff University, Cardiff CF10 3YE, UK (e-mail: LeakeB@cardiff.ac.uk)

⁴Isotope Geosciences Unit, Scottish Universities Environmental Research Centre, East Kilbride, Glasgow G75 0QU, UK

Abstract: Major element compositional analyses, K–Ar ages, δD ‰ and $\delta^{18}O$ ‰ values for 30 zoned and unzoned hornblendes from Dalradian amphibolites and metagabbros, mostly in north Connemara are reported. Although the cooling ages are expected from previous U–Pb zircon studies to be *c.* 475–450 Ma, the results obtained are from 556 ± 6 to 410 ± 9 Ma with an average of 470 Ma. Fluid movements, probably at 275 ± 15 °C, i.e. much below Ar closure temperature for hornblende, erratically reset the ages, as is shown by a negative correlation of hornblende δD and age and a wide scatter of ages even within 2 m. The changes were implemented by H–D exchange between fluid and hornblendes in which ionic porosity, *Z*, influenced the loss of Ar and possibly its gain from the fluid to give the excess Ar found in some samples. *Z* is controlled by hornblende chemical composition. High Mg, Si and Mg/Fe and low Fe, Al, Ti, Na and particularly low K, amphiboles giving low *Z* values retained Ar more firmly and gained Ar more readily than compositions which had higher *Z* values, which gave younger ages. These range down to *c.* 400 Ma, being the age of the intrusion of the Galway Granite suite that initiated the fluid circulation. The scatter of ages is a consequence of incomplete equilibration, mainly because of the slow H–D exchange rate below 350 °C and partly because the fluid permeated erratically in different areas and down cracks of all kinds, promoting irregular Ar movement. The meteoric fluid circulated through Connemara, the Galway Granite and at least some of the contiguous Silurian sediments of the South Mayo trough. These overlying sediments may have contributed to the water circulated in north Connemara which was slightly less negative δD than in central Connemara. For hornblende K–Ar ages to be a reliable measure of times of uplift and cooling, they need to be demonstrated to be free from the influence of hot fluids by showing no correlation of age with δD .

Keywords: Dalradian, Connemara Ireland, K–Ar, hornblende, stable isotopes.

The Dalradian metasediments of Connemara, western Ireland, were metamorphosed and intruded at 470–475 Ma (U–Pb zircon; Friedrich *et al.* 1999a) by a major gabbroic suite. This suite was closely followed by intrusions of calc-alkaline quartz diorite to granite at 467 ± 2 Ma (U–Pb zircon) and by the late magmatic Oughterard Granite, 462.5 ± 1.2 Ma (U–Pb xenotime age; Friedrich *et al.* 1999a, b). The whole intrusive sequence formed part of a short-lived Ordovician continental magmatic arc and is the largest intrusive complex into the Dalradian, being at least 80×26 km (Leake 1989). Peak metamorphism was synchronous with the intrusions at 468–466 Ma followed by a 463–461 Ma (U–Pb titanite) metasomatic event and then rapid cooling between 460 and 450 Ma (Friedrich *et al.* 1999b). Major uplift and southward thrusting of the whole Connemara block was completed by 447 ± 4 Ma based on Rb–Sr isotopic analyses of micas and whole rocks in the Delaney Dome mylonites (Tanner *et al.* 1989). The unconformable deposition of Upper Llandoverly (436–430 Ma; Tucker & McKerrow 1995) sediments and their folding was followed by the major post-tectonic intrusions of the Galway Granite, and its suite of satellite plutons, at *c.* 400 Ma (Leggo *et al.* 1966; Pidgeon 1969). A complete review of the geology of

Connemara has been given by Leake & Tanner (1994) and of South Mayo by Graham *et al.* (1989).

Detailed studies of the K–Ar ages of hornblendes, biotites and muscovites and Rb–Sr age studies of micas from Connemara (Giletti *et al.* 1961; Leggo *et al.* 1966; Moorbath *et al.* 1968; Elias *et al.* 1988; Miller *et al.* 1991), showed that the majority of over 60 hornblendes have ages between 486 ± 10 and 397 ± 8 Ma, with rare samples exceeding 500 Ma, while nearly 90 mica ages similarly fell between 478 ± 9 and 401 ± 7 Ma. Many adjoining samples do not show the expected K–Ar age relationship of hornblende > muscovite > biotite nor are muscovite Rb–Sr ages always greater than Rb–Sr biotite ages. There is no discernible relationship between age and geographic position except that the highly lineated Ballyconneely amphibolite hornblendes, associated with the southward thrusting of Connemara, give K–Ar ages clustered about 460–447 Ma (Leake *et al.* 1983). From plots of elevation (altitude) against K–Ar and Rb–Sr ages of biotites and muscovites, and also K–Ar ages of hornblendes, Elias *et al.* (1988) conclusively excluded the possibility that altitude might be influencing the ages. The puzzling spread of ages over about 100 Ma led Miller *et al.* (1991) to investigate the

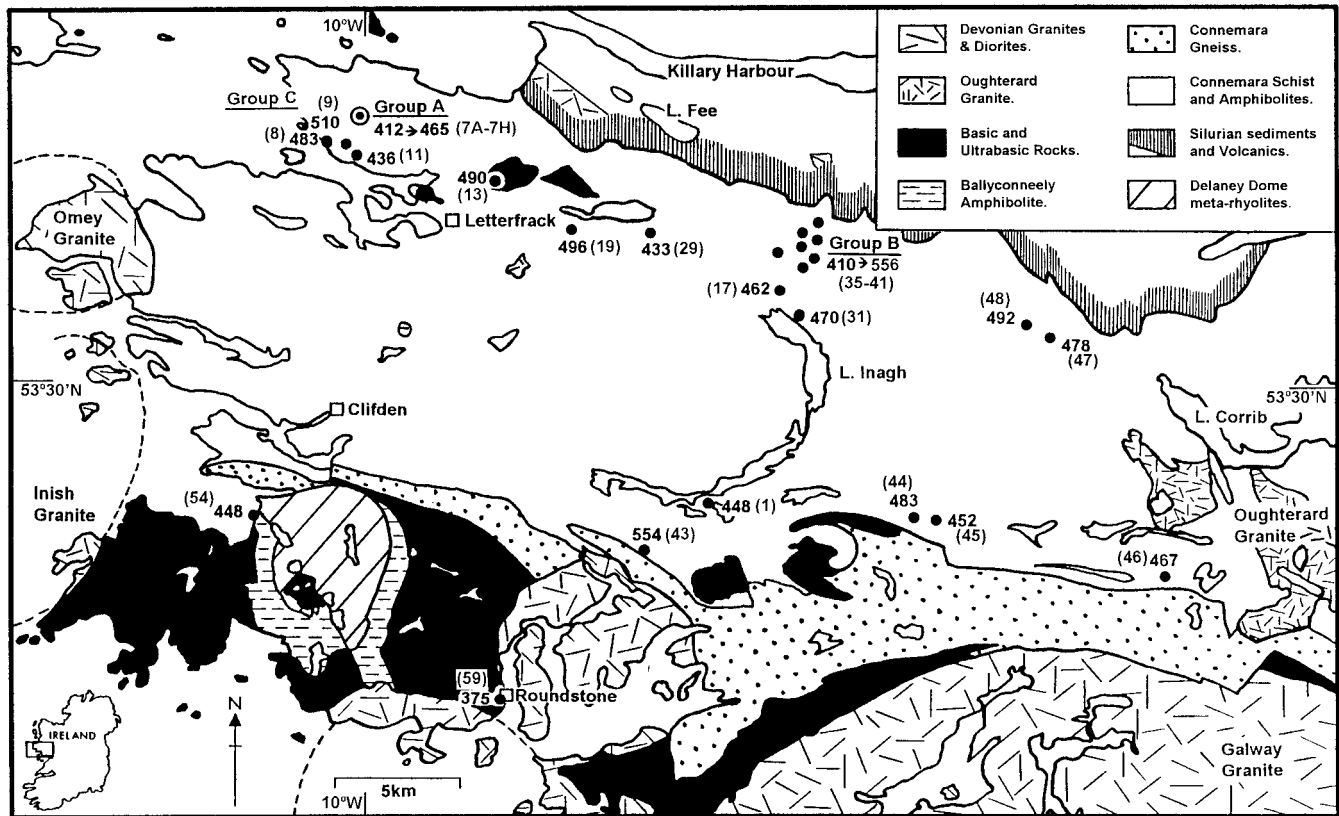


Fig. 1. Map of Connemara, western Ireland, showing the simplified geology, after Leake *et al.* (1981) and Graham *et al.* (1989), the sample locations and K–Ar ages of the analysed hornblendes, separated from amphibolites and metagabbros. Group A samples have a circle with central spot, Group B is a local cluster of seven samples, Group C are three samples SW of Group A. Numbers indicate K–Ar ages in Ma. Sample numbers are in brackets.

relationship between K–Ar ages in Connemara hornblendes and their δD compositions from which it was suggested that fluid interaction related to the Galway Granite intrusions had disturbed the K–Ar system. Subsequent work by Jenkin *et al.* (1992), O'Reilly *et al.* (1997) and Leake (1998) confirmed the widespread retrogression and hydrothermal alteration of minerals by magmatic and meteoric fluids associated with the intrusion of the Galway Granite and its satellite plutons (Roundstone, Inish, Omey and Letterfrack; Fig. 1). Most recently, Friedrich *et al.* (1999b) have suggested that any $^{40}\text{Ar}/^{39}\text{Ar}$ or Rb–Sr dates older than *c.* 468 Ma must reflect isotopic disequilibrium or excess ^{40}Ar contamination and any similar dates younger than *c.* 443 Ma must reflect open-system behaviour unrelated to isotopic closure following metamorphism. From $^{40}\text{Ar}/^{39}\text{Ar}$ studies of muscovite and biotite they deduced that Connemara cooled at $>35^\circ\text{C Ma}^{-1}$ from 468 to 460 Ma and then at $>14^\circ\text{C Ma}^{-1}$ from 460 to 450 Ma and was cold by 443 Ma.

The present work investigates: (1) whether the chemical composition of the hornblende has any influence on the retention of Ar; (2) whether there is evidence of fluid influence on hornblende K–Ar ages in the extreme north of Connemara, as far as possible from the Galway Granite; (3) whether hornblende K–Ar ages show any correlation with the Silurian unconformity and therefore possibly with 'downward' fluid derived from the overlying Silurian sediments. For the last two inquiries, most samples were collected in north Connemara. In aggregate, these studies aim to throw some light on the wide age span of the Connemara hornblendes.

Previous work linking the chemical composition of hornblendes with Ar retention has given conflicting results. O'Nions *et al.* (1969) showed a correlation of composition and K–Ar age but later, on further examination of the same samples, Cosca & O'Nions (1994) concluded there was no correlation. Later, using the data in Cosca & O'Nions (1994) plus the compositional data of O'Nions *et al.* (1969), Dahl (1996) claimed that, with a correlation of $r^2=0.66$, this fitted his ionic porosity (*Z*) model. This monitors atomic packing density, which is related to chemical composition. Dahl (1996) showed that *Z* significantly influences hornblende closure temperatures. Hitherto others (e.g. Onstott & Peacock 1987; Leake *et al.* 1988; Onstott & Pringle-Goodell 1988; Cosca *et al.* 1992) have found no correlation of K–Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ ages and chemical composition in hornblendes. Onstott & Peacock (1987) and Miller (1990) did however recognize that some hornblendes with lowered K–Ar ages contained submicroscopic phyllosilicate alteration, detectable by TEM studies. The present study has included SEM work in addition to chemical and K–Ar analyses and special precautions have been devised to ensure that the determined chemical and isotopic compositions of zoned hornblendes relate to exactly the same material.

Methods

In order to identify closely spaced variations in ages and composition, seven samples (TJ-7A to TJ-7H; Group A) of amphibolite were collected from within a 1.5 m radius in a small roadside quarry north of Tully Mountain; seven amphibolite samples (TJ-35 to TJ-41; Group B) were collected *c.* 2 km north of Lough Inagh with tens of metres

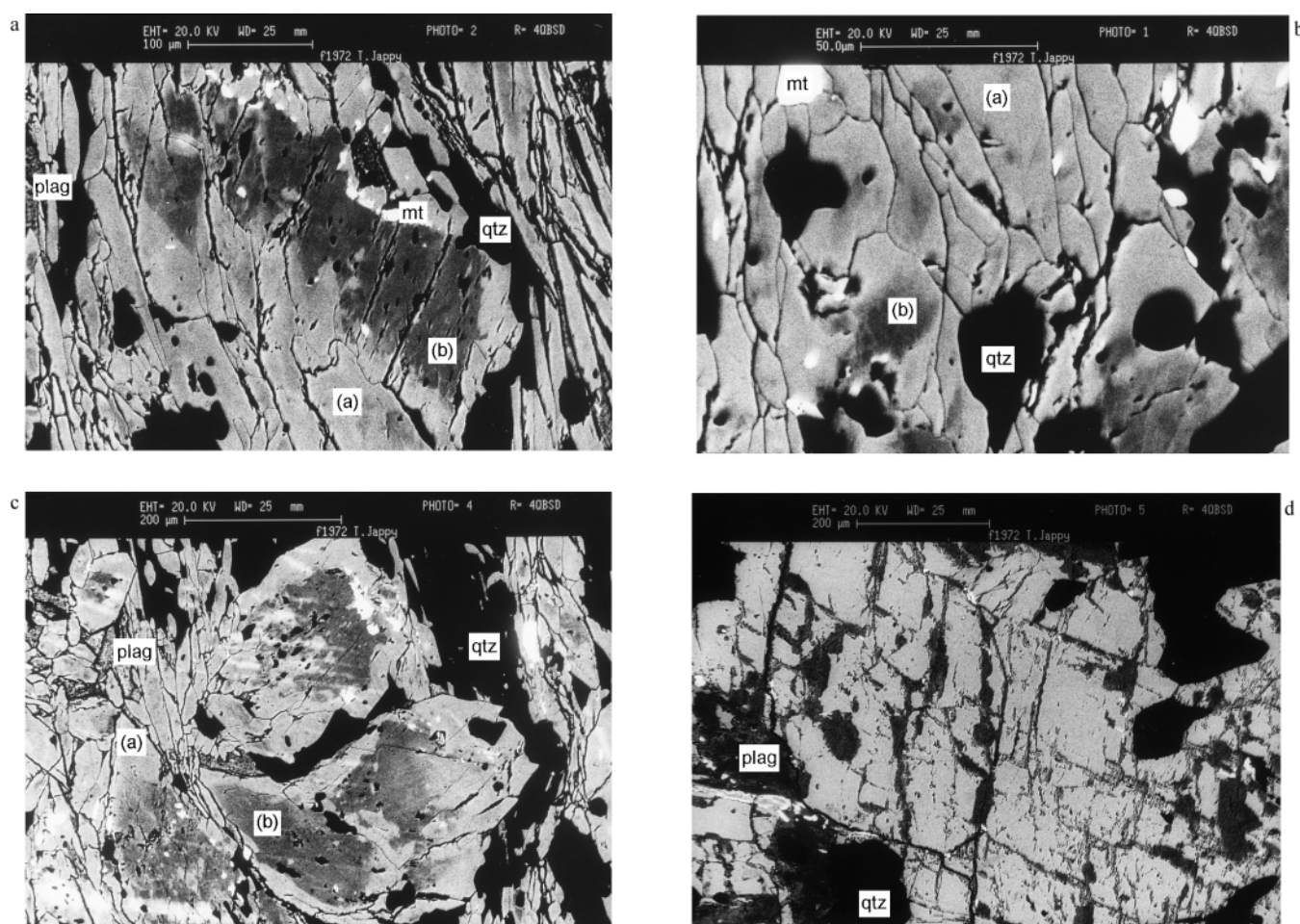


Fig. 2. Scanning electron microscope backscattered electron images of A, B and C zoned hornblendes in sample TJ-7D; lighter rims (a), Al- and Fe-rich; darker cores (b), Si- and Mg-rich; D of uniform hornblende (TJ-44) with alteration to biotite and chlorite along cleavages. Qtz, quartz; plag, plagioclase; mt, magnetite.

between the samples, and three amphibolites (TJ-8, TJ-9 and TJ-11; Group C) tens of metres apart came from south of Tully Mountain. These and other samples are located on Figure 1. Hornblende was separated by magnetic separation and heavy liquids, the purity being at least 98% and was checked optically and by XRD.

The bulk separates of the hornblendes were analysed for Na, Ca, Mg, total Fe and Al using atomic absorption and flame emission spectrophotometry. FeO was determined by KCr_2O_7 titration. Electron microprobe analyses for Si, Ti, Al, Fe, Mn, Mg, Ca, Na and K were obtained at 15 kV and 20 nA on a Cameca SX50 electron probe, using wavelength spectrometry and corrected for atomic number, absorption and fluorescence, at Glasgow University. Backscattered secondary electron (BSE) images of hornblendes in the same polished sections as used for the electron microprobe analyses, were obtained using a Leo Microscopy Stereoscan 360 SEM with an integrated energy dispersive spectrometer. All the isotope work was carried out in the Isotope Geosciences Laboratories of the SUERC, East Kilbride, and involved standard techniques for ^{40}Ar , H and O, as explained in Miller *et al.* (1991) with modifications as given in Jappy (1998). Potassium was determined by flame emission spectrophotometry. Full details of the experimental procedures are given in Jappy (1998). All errors are given at ± 1 standard deviation and the average errors are: K–Ar ages ± 13 Ma; $\delta\text{D} \pm 1.5\%$ and $\delta^{18}\text{O} \pm 0.15\%$ and $\text{H}_2\text{O wt}\% \pm 0.10$.

An important difference between the chemical compositions of the hornblendes given here and those determined by Elias *et al.* (1988) and Miller *et al.* (1991) is that except for K, the previous studies employed only electron microprobe analyses of hornblendes to derive the

average compositions. The zoning and variation of composition (Fig. 2) in some of the amphiboles makes calculation of the average composition very difficult even with careful multiple electron probe analyses. Moreover, because of the separation techniques unavoidably used to create the bulk hornblende concentrates needed for isotopic analysis, it cannot be certain that the hornblende concentrates were exactly the original bulk composition of the zoned hornblende. The least and most magnetic and the lowest and highest density parts could well have been removed. Accordingly, wet chemical analyses were made on the actual bulk hornblende concentrates used for isotopic work for K, Na, Ca, Mg, total Fe and Al, in addition to at least 16–20 complete electron microprobe analyses of amphiboles in each rock. The wet-chemical bulk MgO values were used to calculate the proportions of the extreme microprobe-derived compositions needed to give the average wet-chemical MgO value. These proportions were used to derive the bulk value of elements, like Si, not determined by wet means. Although the amphiboles in north Connemara are more heterogeneous than those farther south, some zoned porphyroblasts are present in some of the southern hornblendes (especially those from the metagabbros). Previous studies have not adequately addressed this problem of accurately obtaining the bulk chemical composition of zoned amphiboles used for dating and other isotopic studies. Fourteen of the hornblendes were uniform in composition and no corrections were applied to the electron microprobe-derived compositions. Following Sachs (1984) the correlation coefficient R is >0.306 for 90% significance and >0.361 for 95% significance on 30 samples (similarly >0.669 and >0.755 for seven samples).

Table 1. Locations, K-Ar ages and stable isotope data for hornblendes

Sample	Grid Reference	K (wt.%)	⁴⁰ Ar* (%)	K-Ar Age (Ma; ± 1 SD)	H ₂ O ⁺ (wt.%)	δD _{HORNBLLENDE} (± 1.5‰)	δD _{FLUID} (± 1.5‰)	δ ¹⁸ O _{HORNBLLENDE} (± 0.15‰)
TJ-1	821467	0.27	73.7	448 ± 10	1.9	-90‰	-67‰	+7.9‰
TJ-7A	672619	0.24	61.9	427 ± 11	1.8	-49‰	-26‰	+8.0‰
TJ-7B	672619	0.42	53.9	412 ± 11	1.6	-45‰	-22‰	+7.1‰
TJ-7D	672619	0.33	68.1	461 ± 11	1.7	-54‰	-31‰	+5.0‰
TJ-7E	672619	0.31	67.5	426 ± 10	1.7	-40‰	-17‰	+6.1‰
TJ-7F	672619	0.33	65.4	465 ± 11	2.0	-57‰	-34‰	+6.5‰
TJ-7G	672619	0.25	59.0	436 ± 11	2.0	-49‰	-26‰	+5.7‰
TJ-7H	672619	0.28	50.0	444 ± 13	2.1	-52‰	-29‰	+8.6‰
TJ-8	660607	0.18	40.9	483 ± 16	2.0	-52‰	-29‰	+6.1‰
TJ-9	665605	0.18	43.5	510 ± 16	2.0	-53‰	-30‰	+4.9‰
TJ-11	669604	0.19	42.7	436 ± 14	1.8	-39‰	-16‰	+5.3‰
TJ-13	722593	0.20	39.2	490 ± 16	2.3	-56‰	-33‰	+7.1‰
TJ-17	832548	0.24	36.9	462 ± 16	1.5	-44‰	-21‰	+6.7‰
TJ-19	751580	0.26	49.9	496 ± 14	2.0	-62‰	-39‰	+6.0‰
TJ-29	782574	0.64	62.6	433 ± 11	2.2	-50‰	-27‰	+6.2‰
TJ-31	835547	0.17	57.2	470 ± 12	2.0	-47‰	-24‰	+7.5‰
TJ-35	838569	0.26	63.3	468 ± 2	1.8	-60‰	-37‰	+7.4‰
TJ-36	839570	0.22	54.2	478 ± 4	2.3	-61‰	-38‰	+7.0‰
TJ-37	839571	0.27	56.5	489 ± 13	1.8	-63‰	-40‰	+7.3‰
TJ-38	838573	0.15	58.0	556 ± 6	2.0	-63‰	-40‰	+8.8‰
TJ-39	839575	0.48	77.2	410 ± 9	2.0	-51‰	-28‰	+7.8‰
TJ-40	835566	0.18	37.9	522 ± 18	2.3	-58‰	-35‰	+7.5‰
TJ-41	820572	0.28	59.3	497 ± 3.5	2.3	-62‰	-39‰	+9.3‰
TJ-43	783465	0.13	48.8	554 ± 16	2.0	-52‰	-29‰	+7.3‰
TJ-44	887467	0.43	53.8	483 ± 13	2.8	-52‰	-29‰	+7.7‰
TJ-45	891465	0.49	60.1	452 ± 11	2.1	-52‰	-29‰	+7.7‰
TJ-46	974449	0.40	62.7	467 ± 11	1.7	-59‰	-36‰	+6.9‰
TJ-47	942530	0.21	54.2	478 ± 13	2.1	-52‰	-29‰	+9.3‰
TJ-48	933537	0.15	43.6	492 ± 15	1.9	-52‰	-29‰	+8.8‰
TJ-54	632466	0.28	44.2	448 ± 14	1.8	-39‰	-16‰	+6.4‰
TJ-59	721398	0.40	50.4	375 ± 11	2.0	-46‰	-23‰	+6.4‰

K-Ar age errors of each sample are based on a single analysis, except TJ-35, TJ-36, TJ-38 and TJ-41, which are based on two analyses (SD given). Average K-Ar age=470 Ma. Average K-Ar age error=± 13 Ma. Single δD analysis for each sample, except TJ-1, TJ-7F, TJ-35, TJ-43 and TJ-44 which are based on two analyses (within errors, averages shown). Average δD=-52‰. Average error for δD=± 1.5‰ (estimated due to method and equipment). Water content (wt.%) of each sample was derived from the yield of H₂. Average hornblende water content=1.96 wt.%. Fluid δD values are derived from the hornblende δ values by the independent fractionation factor of Graham *et al.* (1984):

$$1000\ln\alpha_{\text{HORNBLLENDE-WATER}} = -23.1 \pm 2.5\text{‰}$$

Sample descriptions

All the samples except two (TJ-13 & 59; hornblende-plagioclase metagabbros) are foliated to massive amphibolites, mostly from north Connemara (Fig. 1). They are typically composed of 60–70% partly chloritised hornblende, c. 10–15% variably sericitized and saussuritized plagioclase and 10–15% quartz. Accessory chlorite, magnetite or ilmenite, titanite, apatite, partly chloritized biotite, epidote, pyrite and sometimes cummingtonite, are present. Many of the northern samples (Fig. 1) have zoned hornblendes (Fig. 2) with either light green edges and green to light brown centres or light green cores and darker green margins. Alteration along cleavages to chlorite or minor biotite is common (Fig. 2) and almost all the samples have altered plagioclase. Full descriptions of each sample and its chemical composition are given in Jappy (1998).

Results

The measured K, ⁴⁰Ar, H₂O, δD and δ¹⁸O values of the amphiboles studied and their locations are listed in Table 1, together with the calculated δD value of the fluid in equilibrium with the amphiboles. The average bulk compositions of the actual amphibole fractions studied are given in Table 2 and the extreme (i.e. maximum range) electron microprobe results for those amphiboles which showed a range of composition are

given in Table 3 in order to show the variation involved. According to Leake *et al.* (1997), the formulae given in Table 4 show 22 of the amphiboles in Table 2 are magnesiohornblendes, three are tschermakites, three are pargasites and ferrohornblende, edenite and hastingsite are one each; the general name hornblende is appropriate.

The SEM backscattered electron images of Figure 2 a, b and c (TJ-7D) show the presence of two different compositions within individual amphibole crystals, in this case a zoning effect attributed to later growth of Al- and Fe-rich rims surrounding Si- and Mg-rich cores. This effect is similar to that observed in samples from the late Hercynian orogeny in NE Bavaria (Siebel *et al.* 1998). Figure 2d shows chlorite and biotite replacing hornblende in the cleavages of the amphibole along which fluid must have moved.

Hornblende K-Ar age variations

A wide spread of K-Ar ages has been obtained with extremes at 556 ± 6 Ma and 410 ± 9 Ma, omitting TJ-59 with 375 ± 11 Ma (Table 1 and Fig. 1). There is no correlation of age and geographical or structural position, a conclusion similar to that found in central and southern Connemara. The

Table 2. Bulk compositions from EPMA results

Oxide wt.%	TJ-1	*TJ-7A	*TJ-7B	*TJ-7D	*TJ-7E	*TJ-7F	*TJ-7G	*TJ-7H	*TJ-8	TJ-9	TJ-11
SiO ₂	45.89	45.82	45.66	43.39	45.71	47.08	48.45	45.39	48.06	45.70	45.73
TiO ₂	0.95	0.30	0.28	0.43	0.35	0.16	0.18	0.34	0.24	0.30	0.40
Al ₂ O ₃	9.99	12.03	11.59	12.06	9.78	8.34	7.28	11.44	7.71	13.82	14.16
Fe ₂ O ₃	5.22	3.90	3.63	5.26	4.55	4.01	1.27	3.55	3.41	2.42	2.56
FeO	9.90	12.82	14.47	15.84	14.87	14.40	15.33	13.63	12.43	9.62	9.98
MnO	0.30	0.28	0.27	0.38	0.37	0.34	0.32	0.28	0.34	0.21	0.19
MgO	12.32	9.77	9.28	7.42	0.27	10.73	12.29	10.06	12.29	12.58	11.75
CaO	12.03	11.68	11.36	11.32	11.40	11.82	11.87	11.77	12.54	12.16	11.90
Na ₂ O	1.09	1.08	1.07	1.43	1.26	0.77	0.75	1.17	0.80	1.01	1.16
K ₂ O	0.32	0.34	0.38	0.50	0.41	0.34	0.23	0.39	0.18	0.17	0.20
Total	98.01	98.02	97.99	98.03	97.97	97.99	97.97	98.02	98.00	97.99	98.03
Fe/(Fe+Mg)	0.446	0.568	0.609	0.681	0.616	0.573	0.555	0.575	0.503	0.433	0.459

Oxide wt.%	TJ-13	TJ-17	*TJ-19	*TJ-29	TJ-31	*TJ-35	*TJ-36	*TJ-37	*TJ-38	*TJ-39	*TJ-40
SiO ₂	48.07	44.15	45.45	43.62	47.01	44.11	47.20	45.99	46.51	42.85	45.51
TiO ₂	0.47	0.55	0.35	0.46	0.52	0.40	0.30	0.50	0.31	0.43	0.35
Al ₂ O ₃	8.66	12.46	11.81	12.93	10.92	14.33	11.06	11.06	10.04	13.53	13.85
Fe ₂ O ₃	6.55	3.01	3.95	4.53	2.87	3.08	4.96	3.42	3.24	5.45	2.71
FeO	8.62	14.43	12.42	12.62	10.20	10.58	7.92	12.89	13.20	11.71	9.11
MnO	0.25	0.34	0.31	0.29	0.22	0.29	0.17	0.23	0.32	0.33	0.23
MgO	12.86	9.92	10.51	10.21	12.83	11.84	13.20	10.36	11.37	9.94	13.01
CaO	11.75	10.98	11.51	11.91	12.28	11.79	11.52	12.09	11.90	11.78	11.65
Na ₂ O	0.62	1.84	1.26	1.25	1.05	1.24	1.42	1.08	0.89	1.52	1.34
K ₂ O	0.19	0.31	0.39	0.21	0.14	0.32	0.20	0.39	0.21	0.49	0.24
Total	98.04	97.99	97.96	98.03	98.04	97.98	97.95	98.01	97.99	98.03	98.00
Fe/(Fe+Mg)	0.401	0.593	0.542	0.553	0.443	0.472	0.375	0.554	0.537	0.541	0.412

Oxide wt.%	TJ-41	TJ-43	TJ-44	TJ-45	TJ-46	TJ-47	TJ-48	TJ-54	TJ-59	Average wt.% (SD)
SiO ₂	44.76	48.20	44.24	43.54	44.21	42.71	43.17	40.89	45.90	45.32 (0.83)
TiO ₂	0.34	1.01	0.79	0.63	1.27	0.47	0.41	0.58	0.61	0.47 (0.09)
Al ₂ O ₃	12.85	7.84	11.18	11.52	9.62	13.70	14.23	10.69	9.23	11.28 (0.88)
Fe ₂ O ₃	3.41	3.33	2.85	3.69	5.86	3.35	2.89	8.43	5.90	3.83 (0.04)
FeO	10.85	11.00	13.77	13.82	11.90	11.93	11.47	16.60	10.84	12.09 (0.06)
MnO	0.35	0.22	0.28	0.39	0.35	0.28	0.26	0.48	0.31	0.30 (0.05)
MgO	12.26	13.82	11.13	10.74	11.32	10.94	11.85	6.68	11.80	11.26 (0.57)
CaO	11.74	11.01	11.54	11.13	11.51	12.32	10.43	11.30	12.07	11.68 (0.34)
Na ₂ O	1.20	1.38	1.60	1.93	1.45	2.05	3.06	1.92	1.04	1.31 (0.14)
K ₂ O	0.23	0.16	0.64	0.61	0.50	0.25	0.23	0.41	0.33	0.32 (0.06)
Total	97.99	97.97	98.02	98.00	97.99	98.00	98.00	97.98	98.03	—
Fe/(Fe+Mg)	0.469	0.443	0.553	0.563	0.512	0.522	0.492	0.713	0.479	0.518 (0.016)

EPMA results based on 16–20 point analyses for hornblende samples taken from polished rock sections. The iron measured by EPMA was initially assumed as Fe₂O_{3(total)}. The ratio of Fe₂O₃/FeO as found by wet chemical analysis for each hornblende mineral separate was used to split the measured EPMA Fe₂O_{3(total)} value into the same Fe₂O₃/FeO relative proportions as the mineral separate. The correction Fe₂O_{3(total)} – (FeO × 1.1112) = Fe₂O₃ was also used on this ratio. Fe/(Fe+Mg) in the table is an abbreviation for FeO/(FeO+MgO). In all cases the values were normalized to give a total of 98%, allowing 2% for the presence of H₂O and halogens, which were not analysed in the mineral separates. Samples marked * are representative, bulk compositions of samples which displayed two composition populations as measured by EPMA (Table 3). This bulk composition was estimated by using the MgO value from AAs analysis to calculate a representative intermediate composition (bulk), from compositions (a) and (b) (Table 3). The % ratio of compositions (a) to (b) is given in each case (Table 3).

overall average age is 470 Ma with the 14 (omitting TJ-59) uniform hornblendes ranging from 436 to 554 Ma, averaging 478 Ma, which is insignificantly different from the 410–556 Ma range of the 16 zoned hornblendes, which average 463 Ma. There is age and other variation, well outside determinative

error, on both the scale of about a metre and several kilometres (Fig. 1). The seven samples of Group A, all collected within about 1.5 m of each other, yield 465, 461, 444, 436, 427, 426 and 412 Ma, all *c.* ± 11 Ma (Table 1). Likewise the seven samples of Group B and the three of Group C, all collected

Table 3. EPMA results of samples displaying two hornblende compositions

Oxide wt.%	TJ-7A (a)	TJ-7A (b)	TJ-7B (a)	TJ-7B (b)	TJ-7D (a)	TJ-7D (b)	TJ-7E (a)	TJ-7E (b)
SiO ₂	43.46	45.82	42.98	49.06	42.80	50.70	42.09	51.87
TiO ₂	0.40	0.30	0.41	0.12	0.45	0.20	0.46	0.16
Al ₂ O ₃	14.99	12.03	15.00	7.25	12.57	4.97	13.56	3.34
Fe ₂ O ₃	3.83	3.90	3.65	3.60	5.41	4.46	4.83	4.08
FeO	13.36	12.82	14.57	14.34	15.97	13.76	15.78	13.33
MnO	0.29	0.28	0.27	0.28	0.38	0.40	0.37	0.36
MgO	8.43	9.77	8.05	10.85	7.12	11.27	7.23	12.75
CaO	11.37	11.68	11.26	11.49	11.30	11.41	11.38	11.42
Na ₂ O	1.39	1.08	1.36	0.70	1.47	0.60	1.72	0.48
K ₂ O	0.45	0.34	0.44	0.31	0.51	0.19	0.56	0.16
Total	97.97	98.02	97.99	98.00	97.98	97.96	97.98	97.95
Fe/(Fe+Mg)	0.613	0.568	0.644	0.569	0.692	0.550	0.687	0.511
% from AAS MgO	0%	100%	66%	44%	93%	7%	63%	37%

Oxide wt.%	TJ-7F (a)	TJ-7F (b)	TJ-7G (a)	TJ-7G (b)	TJ-7H (a)	TJ-7H (b)	TJ-8 (a)	TJ-8 (b)
SiO ₂	42.33	47.61	43.65	51.89	43.60	51.06	45.34	48.74
TiO ₂	0.38	0.13	0.39	0.05	0.41	0.12	0.33	0.21
Al ₂ O ₃	13.57	7.76	13.27	3.85	13.51	4.89	11.52	6.71
Fe ₂ O ₃	4.25	3.98	4.05	3.58	3.62	3.34	4.51	2.86
FeO	15.30	14.30	13.18	11.63	13.89	12.82	11.67	12.89
MnO	0.36	0.34	0.26	0.35	0.24	0.39	0.36	0.34
MgO	8.34	11.00	9.61	14.02	9.05	13.25	10.99	12.62
CaO	11.62	11.84	11.93	12.00	11.91	11.33	11.81	12.72
Na ₂ O	1.39	0.70	1.32	0.42	1.36	0.55	1.20	0.69
K ₂ O	0.49	0.32	0.42	0.12	0.45	0.20	0.24	0.17
Total	98.03	97.98	98.08	97.91	98.04	97.95	97.97	97.95
Fe/(Fe+Mg)	0.647	0.565	0.578	0.453	0.605	0.492	0.515	0.505
% from AAS MgO	10%	90%	37%	63%	76%	24%	21%	79%

Oxide wt.%	TJ-19 (a)	TJ-19 (b)	TJ-29 (a)	TJ-29 (b)	TJ-35 (a)	TJ-35 (b)	TJ-36 (a)	TJ-36 (b)
SiO ₂	45.45	49.78	43.23	47.58	44.11	53.19	45.67	51.91
TiO ₂	0.35	0.23	0.47	0.39	0.40	0.15	0.37	0.05
Al ₂ O ₃	11.81	7.63	13.37	8.52	14.33	3.58	12.70	5.04
Fe ₂ O ₃	3.95	3.56	4.58	4.03	3.08	2.52	4.62	5.18
FeO	12.42	11.14	12.76	11.23	10.58	8.63	8.60	7.90
MnO	0.31	0.24	0.30	0.22	0.29	0.22	0.19	0.12
MgO	10.51	12.73	9.97	12.66	11.84	17.27	12.34	16.03
CaO	11.51	12.05	11.87	12.32	11.79	12.06	11.61	11.02
Na ₂ O	1.26	0.43	1.29	0.86	1.24	0.33	1.63	0.66
K ₂ O	0.39	0.18	0.21	0.20	0.32	0.05	0.24	0.08
Total	97.96	97.97	98.05	98.01	97.98	98.00	97.97	97.99
Fe/(Fe+Mg)	0.54	0.46	0.56	0.47	0.47	0.33	0.411	0.330
% from AAS MgO	100%	0%	91%	9%	100%	0%	78%	22%

Continued

decimetres apart, yield ages of 556, 522, 497, 489, 478, 468 and 410 Ma (± 2 –18 Ma), and 510, 483 and 436 Ma (all ± 16 Ma), again showing wide dispersion, but also including samples whose old ages suggest excess ⁴⁰Ar, as discussed below, and whose youngest ages, like those obtained by Elias *et al.* (1988) and Miller *et al.* (1991) match the age of intrusion of the Galway Granite and its satellite plutons at *c.* 400 Ma.

The least disturbed ages appear to be: (1) the metagabbros (Fig. 1) outside the thermal aureole of the Galway Granite of which TJ-13 with 490 ± 16 Ma is the sole present result. When this is added to those of Elias *et al.* (1988) and Miller *et al.* (1991) there are ten samples with hornblende K–Ar ages ranging from 471 to 490 Ma and averaging 479 Ma which is within experimental error of the 470–475 Ma U–Pb zircon ages

Table 3. Continued

Oxide wt.%	TJ-37 (a)	TJ-37 (b)	TJ-38 (a)	TJ-38 (b)	TJ-39 (a)	TJ-39 (b)	TJ-40 (a)	TJ-40 (b)
SiO ₂	45.95	51.10	44.64	50.48	42.85	52.57	45.51	52.91
TiO ₂	0.50	0.15	0.39	0.13	0.43	0.08	0.35	0.13
Al ₂ O ₃	11.04	5.37	12.23	5.40	13.53	3.34	13.85	5.03
Fe ₂ O ₃	2.56	3.18	3.35	3.02	5.45	4.03	2.71	2.43
FeO	13.85	11.96	13.61	12.33	11.71	8.67	9.11	8.19
MnO	0.23	0.32	0.30	0.37	0.33	0.38	0.23	0.21
MgO	10.35	13.16	10.22	13.80	9.94	16.21	13.01	17.44
CaO	12.07	12.03	11.94	11.83	11.78	12.18	11.65	11.11
Na ₂ O	1.08	0.54	1.08	0.49	1.52	0.38	1.34	0.49
K ₂ O	0.39	0.17	0.24	0.16	0.49	0.11	0.24	0.06
Total	98.02	97.98	98.00	98.01	98.03	97.95	98.00	98.00
Fe/(Fe+Mg)	0.572	0.476	0.571	0.472	0.541	0.348	0.412	0.320
% from AAS MgO	100%	0%	68%	32%	100%	0%	100%	0%

These analyses represent the analyses where the EMPA results clustered, even within individual grains. In each case (a) represents a Al-, Ti-, Fe-, Na-, K-rich hornblende and (b) a Si-, Mg-rich hornblende. The bulk composition for each sample (Table 2) is representative of the proportions of compositions (a) and (b) relative to the measured AAS MgO.

For example, TJ-7E:

(a) has 7.23 wt.% MgO

(b) has 12.75 wt.% MgO

AAS=9.28 wt.% MgO

This gives 37% of (a) and 67% of (b)

These proportions are then used to calculate the representative value for each oxide to produce the bulk composition.

of Friedrich *et al.* (1999a); (2) the Ballyconneely amphibolites (Fig. 1) in which the sole present result, TJ-54 with 448 ± 14 Ma is similar to eight other hornblende K–Ar ages (Leake *et al.* 1983) and to a Rb–Sr whole rock dating of the Mannin Thrust at 447 ± 4 Ma (Tanner *et al.* 1989).

Excess argon

Given the U–Pb zircon intrusion ages of the Connemara gabbros as $475\text{--}470 \pm 1$ Ma (Friedrich *et al.* 1999a, b), and the hornblende determinative K–Ar age error is ± 10 to ± 15 Ma (average ± 13) and that there is as yet no reliably determined older ages in Connemara than those of the intrusive gabbro episode, ages greater than 490–500 Ma require critical scrutiny for possible excess ⁴⁰Ar. Influxes of excess Ar are known from many areas (e.g. Lee *et al.* 1990). Four hornblendes (TJ-9, TJ-38, TJ-40 and TJ-43) yield ages exceeding 500 Ma and range from 510 ± 16 to 556 ± 6 Ma and all occur in samples with very low K contents (0.18, 0.15, 0.18 and 0.13 wt.% K; Fig. 3); only two other samples have ≤ 0.18 wt.% K and one of these (TJ-48) yields 492 ± 16 Ma. This seems to confirm that excess ⁴⁰Ar has infiltrated some samples and although only convincingly detected in the low K samples (where a small addition of ⁴⁰Ar makes a large change), excess ⁴⁰Ar may be present in some of the remaining samples. It is unlikely that excess Ar is a major factor in most of the hornblendes because their age range of 400–490 Ma matches closely that given by over 100 K–Ar ages on muscovites and biotites (including ⁴⁰Ar/³⁹Ar ages) in which excess Ar was extremely rare (Elias *et al.* 1988; Miller *et al.* 1991; Jappy 1998). The source of this excess Ar might be in fluid inclusions and could well have been Ar removed in fluids from other minerals including hornblende. Although there is no correlation of age (or δD) and degree of A-site filling so the excess Ar is not necessarily located in otherwise empty A-sites, the variable 0–1.0 filling of the A-site in hornblendes precludes a decisive conclusion. It

also frustrates evaluation of the alternative to excess Ar, namely fluid removal of K, resulting in an association of low K with older ages. This last possibility is rejected because TJ-38 and TJ-48 with ages of 556 and 522 Ma have K-poor centres and K-richer margins to zoned crystals, which does not support fluid removal of K.

Correlation of K–Ar age and composition

The results shown in Figures 3 & 4 reveal correlation of hornblende K–Ar age with FeO, MgO, Mg/(Mg+Fe)= Mg#, K₂O, δD and more doubtfully with water content such that the oldest ages occur in the hornblendes that have high MgO, Mg# and possibly water and low Fe, K and δD . These results seem generally consistent with Dahl's (1996) proposal that one control on the diffusivity of neutral species (such as ⁴⁰Ar, He and O as in water) is the ionic porosity, Z, of a mineral. This is a measure of atomic packing density and is defined as the percentage of the unit cell volume not occupied by ions (i.e. empty space) so that $Z\% = [1 - (V_i/V_c)] \times 100$ where V_i is the total volume of ions in the unit cell and V_c is the unit cell volume at a particular temperature. Dahl (1996) also modelled the closure temperature of Ar, He and O (if it diffuses as water) as some 60 ± 10 °C higher for Mg-rich hornblendes than Fe-rich ones, some 40 ± 15 °C higher for amphiboles with full A-sites (i.e. K, Na and perhaps H₃O⁺) than empty A-sites and c. 38 °C higher as Al enters tremolite converting it to tschermakite. Ti also lowers closure temperature. The complex chemical variations of hornblendes, which chemical analyses show to be related to rock composition (Jappy 1998), often obscure the influence of one single chemical variation. Figure 3c shows that the oldest ages occur in hornblendes with the lowest Z, i.e. the lowest empty space or the greatest packing density. Even if all ages >490 Ma are omitted on the grounds of excess Ar, there is still a decrease of K–Ar age with increase of Z, i.e. empty space. The scatter on the Z plot is presumably

Table 4. Hornblende mineral formulae calculated from the EPMA results of Table 2 on the basis of 23 oxygens per formula unit by the method outlined by Deer et al. (1966)

	Cation	TJ-1	TJ-7A	TJ-7B	TJ-7D	TJ-7E	TJ-7F	TJ-7G	TJ-7H
T-site (8)	Si	6.68	6.72	6.73	6.53	6.81	6.96	7.03	6.69
	Al ^{IV}	1.32	1.28	1.27	1.47	1.19	1.04	0.97	1.31
C-site (5)	Al ^{VI}	0.39	0.80	0.75	0.66	0.53	0.42	0.28	0.67
	Ti	0.11	0.04	0.04	0.05	0.04	0.02	0.02	0.04
	Fe ³⁺	0.58	0.42	0.41	0.59	0.50	0.44	0.14	0.39
	Mg	2.68	2.13	2.04	1.66	2.06	2.36	2.66	2.21
	Fe ²⁺	1.21	1.57	1.76	1.99	1.85	1.76	1.86	1.68
	Mn	0.03	0.04	—	0.05	0.02	—	0.04	0.01
	B-site (2)	Fe ²⁺	—	—	0.02	—	—	—	—
Mn		0.01	—	0.04	—	0.03	0.04	—	0.03
Ca		1.88	1.83	1.80	1.82	1.82	1.87	1.84	1.86
Na		0.11	0.17	0.14	0.18	0.15	0.09	0.16	0.11
A-site (0–1)	Na	0.20	0.13	0.16	0.23	0.21	0.12	0.05	0.23
	K	0.05	0.07	0.07	0.09	0.07	0.07	0.03	0.07
Z (%)		37.75	37.90	37.93	37.98	37.92	37.91	37.97	37.83

	Cation	TJ-8	TJ-9	TJ-11	TJ-13	TJ-17	TJ-19	TJ-29	TJ-31
T-site (8)	Si	7.03	6.56	6.57	6.93	6.53	6.66	6.43	6.80
	Al ^{IV}	0.97	1.44	1.43	1.07	1.47	1.34	1.57	1.20
C-site (5)	Al ^{VI}	0.36	0.91	0.97	0.40	0.70	0.70	0.68	0.66
	Ti	0.03	0.03	0.04	0.05	0.06	0.04	0.05	0.03
	Fe ³⁺	0.37	0.26	0.28	0.71	0.34	0.44	0.50	0.31
	Mg	2.68	2.69	2.52	2.76	2.19	2.30	2.24	2.76
	Fe ²⁺	1.52	1.11	1.19	1.04	1.71	1.52	1.53	1.23
	Mn	0.04	—	—	0.04	—	—	—	0.01
	B-site (2)	Fe ²⁺	—	0.05	0.01	—	0.08	—	0.03
Mn		—	0.03	0.03	—	0.04	0.04	0.04	0.02
Ca		1.97	1.87	1.83	1.82	1.74	1.81	1.88	1.90
Na		0.03	0.05	0.13	0.18	0.14	0.15	0.05	0.08
A-site (0–1)	Na	0.20	0.23	0.20	—	0.39	0.20	0.30	0.22
	K	0.04	0.03	0.03	0.03	0.05	0.07	0.04	0.03
Z (%)		37.78	37.67	37.73	37.83	37.75	37.81	37.84	37.69

	Cation	TJ-35	TJ-36	TJ-37	TJ-38	TJ-39	TJ-40	TJ-41	TJ-43
T-site (8)	Si	6.40	6.77	6.75	6.82	6.33	6.53	6.52	6.98
	Al ^{IV}	1.60	1.23	1.25	1.18	1.67	1.47	1.48	1.02
C-site (5)	Al ^{VI}	0.86	0.62	0.66	0.55	0.69	0.88	0.72	0.32
	Ti	0.04	0.03	0.05	0.04	0.04	0.03	0.04	0.11
	Fe ³⁺	0.33	0.53	0.29	0.35	0.60	0.29	0.37	0.37
	Mg	2.57	2.82	2.27	2.49	2.19	2.79	2.66	2.99
	Fe ²⁺	1.20	0.98	1.70	1.57	1.45	1.01	1.21	1.21
	Mn	—	0.02	0.03	—	0.03	—	—	—
	B-site (2)	Fe ²⁺	0.08	—	—	0.05	—	0.09	0.11
Mn		0.04	—	—	0.04	0.01	0.03	0.05	0.03
Ca		1.83	1.77	1.91	1.87	1.86	1.79	1.83	1.71
Na		0.05	0.23	0.09	0.04	0.13	0.09	0.01	0.14
A-site (0–1)	Na	0.30	0.17	0.21	0.21	0.31	0.29	0.32	0.24
	K	0.05	0.03	0.07	0.04	0.09	0.05	0.03	0.03
Z (%)		37.72	37.66	37.84	37.81	37.78	37.58	37.65	37.68

The number of cations for each site are given in brackets. Z is ionic porosity.

Continued

Table 4. Continued

	Cation	TJ-44	TJ-45	TJ-46	TJ-47	TJ-48	TJ-54	TJ-59
T-site (8)	Si	6.54	6.48	6.56	6.30	6.32	6.29	6.73
	Al ^{IV}	1.46	1.52	1.44	1.70	1.68	1.71	1.27
C-site (5)	Al ^{VI}	0.50	0.50	0.23	0.67	0.78	0.22	0.33
	Ti	0.09	0.07	0.14	0.05	0.04	0.06	0.07
	Fe ³⁺	0.32	0.41	0.66	0.37	0.32	0.98	0.65
	Mg	2.45	2.38	2.50	2.40	2.59	1.53	2.58
	Fe ²⁺	1.64	1.64	1.47	1.47	1.27	2.14	1.33
	Mn	—	—	—	0.04	—	0.07	0.04
B-site (2)	Fe ²⁺	0.07	0.08	0.01	—	0.14	—	—
	Mn	0.04	0.05	0.05	—	0.04	—	—
	Ca	1.83	1.77	1.83	1.95	1.64	1.86	1.90
	Na	0.06	0.10	0.11	0.05	0.18	0.14	0.10
A-site (0–1)	Na	0.40	0.45	0.30	0.53	0.68	0.43	0.20
	K	0.12	0.11	0.09	0.05	0.04	0.07	0.05
Z (%)		37.63	37.72	37.67	37.65	37.53	37.98	37.74

a consequence of the ideal conditions for control of age of closure by *Z* being violated by: (1) the cooling taking place under 'wet' conditions with some tectonism instead of under 'dry' and static conditions; (2) the irregular presence of extraneous argon; (3) the textural variation of the samples, many of which contain a wide range of amphibole grainsizes; incipient replacement by phyllosilicates and structural defects, all of which reduce effective grainsize; (4) partial reheating by hot fluid circulation (see below), the effects of which in lowering the K–Ar ages become stronger as *Z* increases as Ar is held less tightly with increase of *Z* (Dahl 1996) and possibly also the mineral becomes more susceptible to alteration. Figure 4c is a plot of δD and *Z*; for the data in Tables 1 and 4 the correlation is not statistically significant ($R=0.2296$ for $n=31$).

Correlation of K–Ar ages and fluid movement

Figure 4b shows a repetition (with >99.9% confidence for the data in Table 1) of the negative correlation of δD with age first recognised by Miller *et al.* (1991) as indicative of fluid-disturbed ages. Although, as detailed above, chemical composition and *Z* have some influence on the age pattern, fluid activity is more important. This is shown by both the higher statistical correlation of δD and age and also the wide scatter of K–Ar ages within small areas, as detected within Groups A, B and C for hornblendes, and as reported by Miller *et al.* (1991) for hornblendes, muscovites and biotites. The most likely cause of such age scatter is heterogeneous fluid movement along cracks, veins, joints, foliation and cleavage planes disturbing the ages but not normally reaching equilibrium. Ar was removed from some grains, especially those with higher *Z* values and added (at the same time?) to others in a complex manner that only $^{40}\text{Ar}/^{39}\text{Ar}$ studies might clarify. The cause of the fluid circulation is ascribed to the intrusion of the Galway Granite suite because the youngest K–Ar ages of hornblendes, biotites and muscovites approach *c.* 400 Ma, the age of intrusion of this suite and because the Galway Granites show abundant evidence of interaction with meteoric fluids.

Jenkin *et al.* (1992) and O'Reilly *et al.* (1997) have shown that most of the mineralogical alteration in Connemara took place at 275 ± 15 °C (although higher and lower temperature fluids have been present) due to a meteoric fluid which had $\delta^{18}\text{O} \approx 10\text{‰}$ and from measured fluid inclusions had δD of

– 19‰. It is estimated that this fluid started with δD of – 22 to – 30‰ and $\delta^{18}\text{O} \approx -4\text{‰}$ the latter being significantly modified by exchange with silicates. Using Graham *et al.*'s (1984) relationship, the calculated δD of the fluids in equilibrium with the hornblendes whose δD have been determined are given in Table 1 and plotted in Figure 5, demonstrating that the calculated fluids broadly agree with the compositions independently deduced by O'Reilly *et al.* (1997). The maximum temperature of the fluid, 340 °C (Jenkin *et al.* 1992), is well below the Ar closure temperature of $550\text{--}500 \pm 50$ °C in hornblendes (Harrison 1981). Graham *et al.* (1984) showed that H–D exchange below 350 °C was very slow and this accounts for some of the scatter of ages as complete equilibrium was not achieved.

Figure 3d suggests a positive correlation of H₂O wt.% with K–Ar age but this is rejected because: (1) despite being 90% significant with $R=0.354$, this is the lowest correlation of any of the plots in Figures 3 and 4 except Figure 4c which is not significant; (2) Miller *et al.* (1991) obtained the opposite result with youngest ages having the highest water contents; (3) since there are negative correlations of δD and H₂O wt% (Fig. 4a) and of δD and K–Ar age (Fig. 4b), a negative correlation of age and water content is expected; (4) O'Reilly *et al.* (1997) showed a marked increase in the abundance of hydrous fluid inclusions as alteration proceeded in the Galway Granite. The theoretical water content of a F- and Cl-free hornblende ranges from 2.0 to 2.1 wt% H₂O, so that Miller *et al.*'s (1991) amphiboles which ranged from 1.83 to 2.99 wt% H₂O (average 2.39 wt%) suggest phyllosilicate alteration (chlorite has *c.* 12 wt% H₂O; biotite >4 wt% H₂O) possibly with some increase of fluid inclusions or minor entry of excess H₂O, possibly as H₃O⁺, into the vacant space. Other studies have demonstrated younger ages in altered minerals with older ages being retained in least altered minerals, e.g. biotite (Roberts *et al.* 2001). The present results have a smaller range and lower level of water content than Miller *et al.* (1991), ranging from 1.5 to 2.3 wt% H₂O, average 1.96 ± 0.10 wt% (average error), reflecting in part the rigorous removal of most of the phyllosilicate-altered amphibole. As the same age range *c.* 400–490 Ma occurs in the present samples as those of Miller *et al.* (1991), it suggests that the prime mechanism causing loss of Ar is not phyllosilicate alteration alone but irregular fluid penetration along cracks of all kinds, promoting H–D exchange with the hornblende and

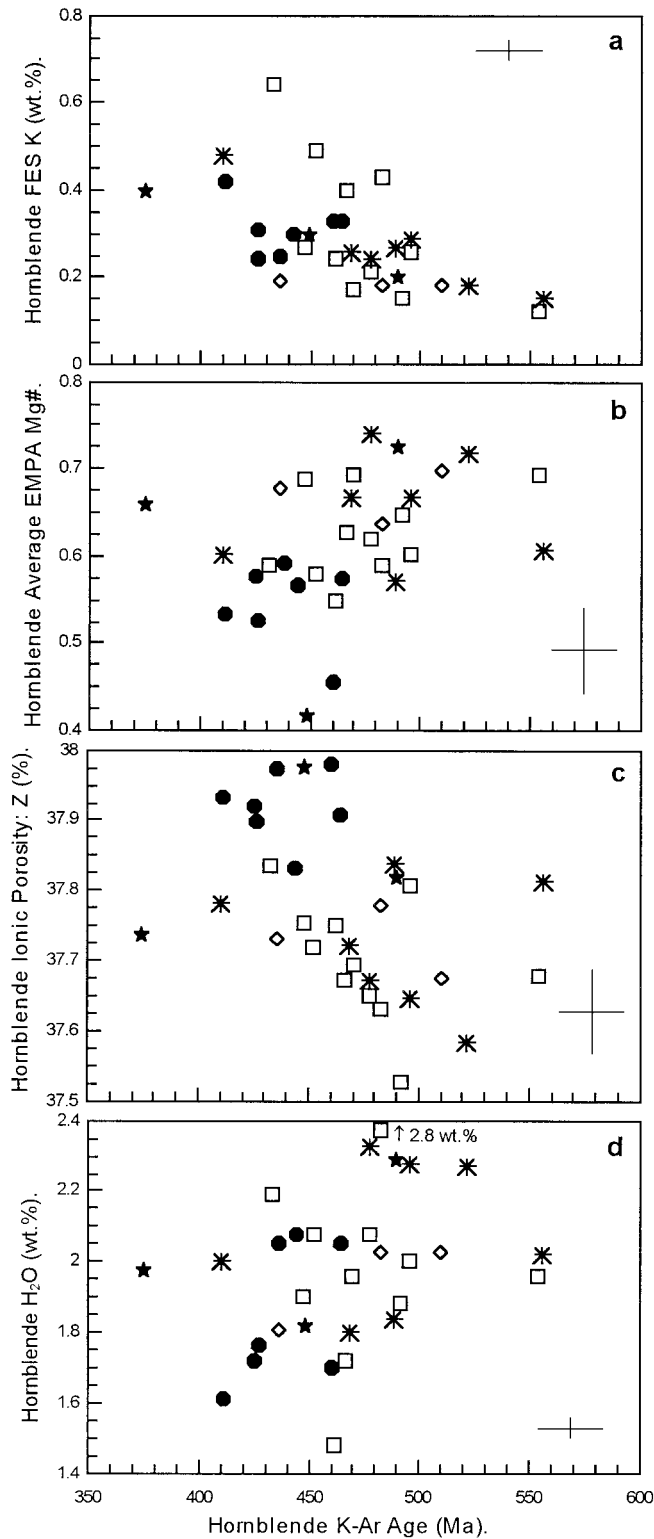


Fig. 3. Comparisons of hornblende K-Ar ages with: (a) Flame emission spectrophotometer (FES) determined K wt.%; R for whole dataset = -0.576 ($>99\%$ significance); for Group B = -0.914 ($>99\%$ significance); (b) Electron microprobe analysed (EMPA) $MgO/(MgO+FeO)$; $R=0.525$ ($>99\%$ significance); (c) Ionic Porosity, Z %; $R=-0.487$ ($>99\%$ significance); (d) H_2O wt.%. Amphibolites; Group A, filled circles; Group B, asterisks; Group C, open diamonds; others, open squares. Metagabbros, filled stars; R , 0.354 (90–95% significance). Error bars are at ± 1 standard deviation.

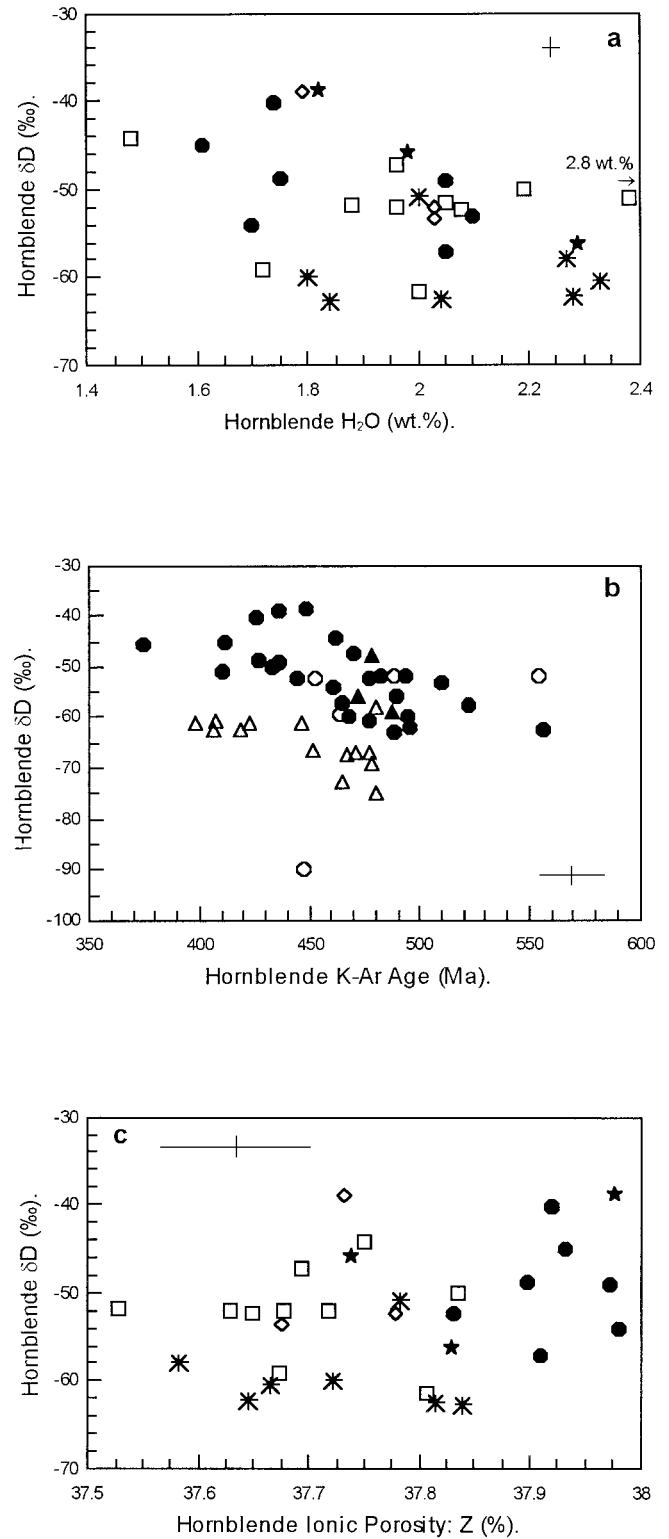


Fig. 4. Comparisons of hornblende δD values (‰) with: (a) H_2O wt.%; $R=-0.371$ ($>95\%$ significance); (b) hornblende K-Ar ages: Results from central and northern Connemara shown as open and filled circles respectively. Present data have $R=-0.582$ ($>99.9\%$ significance); Results of Miller *et al.* (1991) from central and northern Connemara shown as open and filled triangles respectively, clearly a similar trend is in Miller's data but with a lower δD in the central area. (c) Ionic Porosity, Z; $R=0.230$ which is not significant. Error bars are at ± 1 standard deviation.

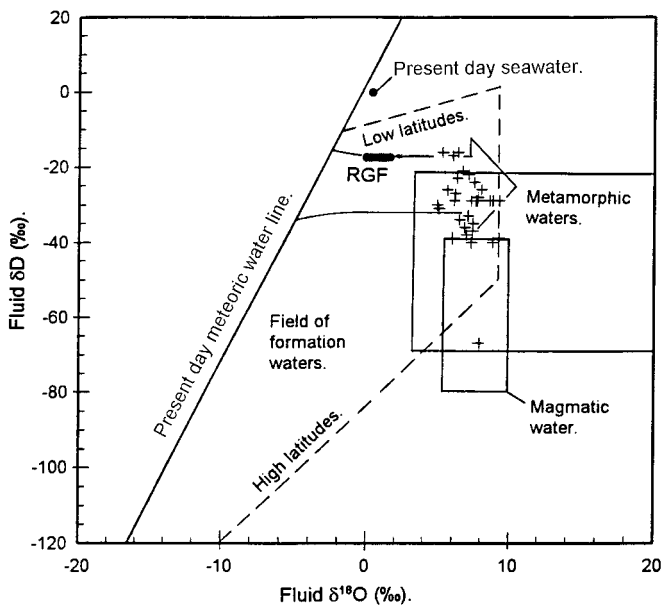


Fig. 5. Calculated fluid δD (crosses) derived from hornblende δD plotted against fluid $\delta^{18}O$ assuming hornblende $\delta^{18}O$ equals fluid $\delta^{18}O$. RGF is the measured retrograde fluid (in fluid inclusions) of Jenkin *et al.* (1997), and the open arrow indicates the deduced change in meteoric water composition as it moved through the Connemara rocks, taken from O'Reilly *et al.* (1997).

concomitant removal of Ar, resulting in the correlation of δD and age. The release of the Ar (and its capture) is related to the firmness with which it is held, i.e. is a function of Z .

Discussion

The samples collected farthest from the Galway Granite, those of Group B (Fig. 1), are no less than 13 km from the nearest edges of the Roundstone and Letterfrack Granites and 16 km from the nearest margin of the Galway Granite, especially as gravity and other evidence (Leake & Tanner 1994) indicates steep edges to these granites. However, intruding the Silurian rocks near Lough Fee, about 7 km WNW of the Group B samples, are a number of diorite intrusions, up to 4×1 km in area, the nearest exposure of which to the Group B samples is a small body, less than 1 km² in area which is about 1 km away. These diorites are post-Wenlock and pre-Carboniferous (Graham *et al.* 1989) and probably belong to the same Lower Devonian magmatic episode as the Galway Granite. Attempts to separate hornblende from these diorites to date them failed utterly because of the intensive alteration of the hornblende to chlorite and epidote. Hydrous decomposition of the plagioclase is ubiquitous. Clearly these diorites suffered very severe fluid movement and the implication is that the hydrothermal systems set up by the widespread intrusion of Lower Devonian magmas in Connemara merged into each other and formed a large complex interacting system which seems to have affected all Connemara, as originally supposed by Jenkin *et al.* (1992). Thus Friedrich *et al.*'s (1999a) determination of the age of the Oughterard Granite (mostly in eastern Connemara, Fig. 1) at 462.5 ± 1.2 Ma, using U–Pb in xenotime, shows that the 407 ± 23 Ma Rb–Sr error-chron of the age of the granite by Kennan *et al.* (1987) was actually dating the intensive and extensive alteration of the granite by fluids driven by the cooling Galway Granite. So virtually all the exposed Connemara massif, all the Galway Granite (Leake 1998) and even some of the South

Mayo trough sediments, with their intensely altered diorite, contain evidence of a *c.* 400 Ma fluid movement event extending over a total area $>80 \times 45$ km. Still later alteration of at least some of the area at 305 Ma and 210 Ma has been established by Jenkin *et al.* (1997), but the last two events are not recorded in the present data because only one hornblende has an age below 400 Ma, TJ-59 with 375 ± 11 Ma which comes from the aureole of the Roundstone Granite (Fig. 1).

Comparison of the age versus δD plot (Fig. 4b) for the present data and that of Miller *et al.* (1991), a total of 49 hornblendes, shows that there is a tendency to plot in two distributions corresponding to central Connemara, which ranges from -52 to -90 ‰, and to northern Connemara ranging from -39 to -63 ‰. Graham *et al.* (1984) showed that down to at least as low as 350 °C, the fractionation factor of normal hornblende with contiguous water is independent of temperature. Assuming that the investigated hornblendes behaved as those studied by Graham *et al.* (1984), then the amphiboles in the north may have equilibrated with a water of slightly less negative δD , average -32 ± 5 ‰, than that which the amphibolites in central Connemara equilibrated with, which averages -40 ± 6 ‰. Considering only the present samples and those of Miller *et al.* (1991) which come from within 3 km of the unconformity underlying the Silurian rocks lying to the north, gives a total of 14 hornblendes which give the same average fluid composition of $\delta D -32 \pm 4$ ‰. The slightly less negative northern δD fluid may result from meteoric water containing a contribution of water driven out of the Silurian sediments, which must have overlain north Connemara before erosion stripped off the sediments.

While the reasons why the metagabbros and Ballyconneely Amphibolites have retained their original ages are uncertain, it may be connected with the very low Z values of the Mg-rich and K-poor hornblendes in the metagabbros and the dense, lined, highly sheared and relatively impermeable nature of the Ballyconneely Amphibolites.

Conclusions

Except for the hornblende K–Ar ages of the metagabbros (average 479 ± 10 Ma) and the Ballyconneely Amphibolites (average 448 ± 14 Ma) which seem to have retained original cooling ages, the remainder of the Connemara hornblendes, whose K–Ar ages range from 410 to 556 Ma, had their initial cooling ages erratically modified by heated meteoric fluid circulated by the heat from the *c.* 400 Ma Galway Granite Suite. This is shown by the negative correlation of hornblende δD and age, general reduction in K–Ar ages and a wide scatter of ages between nearby samples. The changes were implemented by H–D exchange between fluid and hornblendes in which ionic porosity, Z , which is largely controlled by the chemical composition of the hornblendes, influenced the loss of Ar, and possibly its gain from the fluid, to give the excess Ar found in some samples. High Si, Mg and Mg# and low Al, Ti, Na and particularly low K amphibolites with low Z (little empty space) retained Ar more firmly, and gained Ar more readily, than other compositions with higher Z (more empty space) which gave younger ages. Although chlorite and biotite alteration of hornblende by fluid was extensive, this was not the sole or most important means of H–D exchange and Ar movement. The scatter of ages down to *c.* 400 Ma is a consequence of incomplete equilibrium being achieved, mainly because of the very slow H–D exchange rate below 350 °C (Graham *et al.* 1984) and partly because the fluid permeated erratically in different areas and down cracks of all kinds

including cleavages, phyllosilicate alterations and structural discontinuities. This promoted irregular Ar movement. The hot fluids, estimated by Jenkin *et al.* (1992) to be 275 ± 15 °C for most of the retrogressive activity, were much cooler, by >160 °C, than the normal Ar isotope closure temperature of $500\text{--}550 \pm 50$ °C in hornblendes. For hornblende K–Ar ages to be a reliable measure of time of uplift and cooling, they need to be demonstrated to be free from the influence of hot fluids by showing no correlation of age with δD .

The Connemara region, extending over several thousand km², has suffered massive hot water circulation, largely meteoric in source, but possibly in northern Connemara, including a contribution of water from the overlying Silurian sedimentary rocks.

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