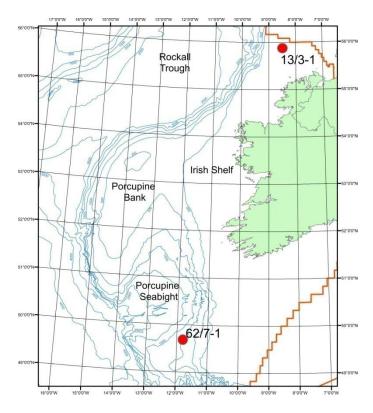


# Geochronology of volcanic rocks from the Irish Shelf

Marine Geoscience Programme Commissioned Report CR/09/018



Report to the Petroleum Affairs Division, Department of Communications, Energy and Natural Resources, Dublin, Ireland.

Based on samples provided by PAD.

Confidential

MARINE GEOSCIENCE PROGRAMME COMMISSIONED REPORT CR/09/018

# Geochronology of volcanic rocks from the Irish Shelf

Darren Mark<sup>1</sup>, Ian L Millar<sup>2</sup>, Kenneth Hitchen<sup>3</sup>

The National Grid and other Ordnance Survey data are used with the permission of the Controller of Her Majesty's Stationery Office. Licence No: 100017897/ 2010.

Keywords
Isotopes, Offshore Ireland.

Front cover

Location map of the two wells sampled on the Irish Shelf

Bibliographical reference

MARK, D, MILLAR, IL AND HITCHEN, K. 2010. Geochronology of volcanic rocks from the Irish Shelf. *British Geological Survey Commissioned Report*, CR/09/018. 12pp.

Copyright in materials derived from the British Geological Survey's work is owned by the Natural Environment Research Council (NERC) and/or the authority that commissioned the work. You may not copy or adapt this publication without first obtaining permission. Contact the **BGS Intellectual Property Rights** Section, British Geological Survey, Keyworth, e-mail ipr@bgs.ac.uk. You may quote extracts of a reasonable length without prior permission, provided a full acknowledgement is given of the source of the

Maps and diagrams in this book use topography based on Ordnance Survey mapping.

- <sup>1</sup> NERC Argon Isotope Facility, Scottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, East Kilbride, G75 0QF, Scotland, UK
- NERC Isotope Geosciences Laboratory, Keyworth, Nottingham, NG12 5GG, UK
- <sup>3</sup> British Geological Survey, Murchison House, West Mains Road, Edinburgh, EH9 3LA, UK

Keyworth, Nottingham British Geological Survey 2010

#### **BRITISH GEOLOGICAL SURVEY**

The full range of our publications is available from BGS shops at Nottingham, Edinburgh, London and Cardiff (Welsh publications only) see contact details below or shop online at www.geologyshop.com

The London Information Office also maintains a reference collection of BGS publications, including maps, for consultation.

We publish an annual catalogue of our maps and other publications; this catalogue is available online or from any of the BGS shops.

The British Geological Survey carries out the geological survey of Great Britain and Northern Ireland (the latter as an agency service for the government of Northern Ireland), and of the surrounding continental shelf, as well as basic research projects. It also undertakes programmes of technical aid in geology in developing countries.

The British Geological Survey is a component body of the Natural Environment Research Council.

British Geological Survey offices

#### **BGS Central Enquiries Desk**

Tel 0115 936 3143 Fax 0115 936 3276

email enquiries@bgs.ac.uk

#### Kingsley Dunham Centre, Keyworth, Nottingham NG12 5GG

Tel 0115 936 3241 Fax 0115 936 3488

email sales@bgs.ac.uk

#### Murchison House, West Mains Road, Edinburgh EH9 3LA

Tel 0131 667 1000

Fax 0131 668 2683

email scotsales@bgs.ac.uk

#### Natural History Museum, Cromwell Road, London SW7 5BD

Tel 020 7589 4090 Fax 020 7584 8270

Tel 020 7942 5344/45 email bgslondon@bgs.ac.uk

## Columbus House, Greenmeadow Springs, Tongwynlais, Cardiff CF15 7NE

Tel 029 2052 1962 Fax 029 2052 1963

### Forde House, Park Five Business Centre, Harrier Way, Sowton EX2 7HU

Tel 01392 445271 Fax 01392 445371

## Maclean Building, Crowmarsh Gifford, Wallingford OX10 8BB

Tel 01491 838800 Fax 01491 692345

## Geological Survey of Northern Ireland, Colby House, Stranmillis Court, Belfast BT9 5BF

Tel 028 9038 8462 Fax 028 9038 8461

www.bgs.ac.uk/gsni/

Parent Body

# Natural Environment Research Council, Polaris House, North Star Avenue, Swindon SN2 1EU

Tel 01793 411500

Fax 01793 411501

www.nerc.ac.uk

Website www.bgs.ac.uk

Shop online at www.geologyshop.com

# Acknowledgements

Ms. Nicola White is thanked for help with the U-Pb analyses. The authors also gratefully acknowledge the members of the BGS Rockall Consortium and the BGS – NIGL programme who funded this research project.

We are particularly indebted to Noel Murphy and Michael Hanrahan (both of PAD) for allowing access, and facilitating sampling, of the core material.

## Contents

Ack	knowledge	ements	i
Cor	ntents		i
Sun	nmary		ii
1	Introduct	ion	1
2	2.1 Me	ethodologyta	1
3	U-Pb geo	ochronology	5
4	Discussion	on	5
Ref	erences		6
FIG	URES		
Fig	ure 1.1	Ar-Ar age spectrum, K/Ca ratios and percentage of radiogenic <sup>40</sup> Ar released during each step for sample 62/7-1 (packet 37)	4
Fig	ure 1.2	Inverse isochron plot constructed using accepted steps from age spectrum for sample 62/7-1 (packet 37).	4
Fig	ure 1.3	Ar-Ar age spectrum, K/Ca ratios and percentage of radiogenic <sup>40</sup> Ar released during each step for sample 62/7-1 (packet 48)	4
Fig	ure 1.4	Inverse isochron plot constructed using accepted steps from age spectrum for sample 62/7-1 (packet 48).	5
TA	BLES		
Tab	ole 1	Ar isotope data for sample 62/7-1 (packet 37)	2
Tab	ole 2	Ar isotope data for sample 62/7-1 (packet 48)	3
Tab	ole 3	U-Pb data for pyrite and apatite separates from 13/3-1	6

## **Summary**

This report contains the results of Ar-Ar geochronological analysis of a sample of igneous rock from well 62/7-1, drilled to the south-west of Ireland. An average age of  $93.8 \pm 1.0$  Ma was derived from the weighted mean of the two plateau ages for this sample. The report also documents an unsuccessful attempt to date an igneous sample from well 13/3-1, to the north of Ireland, using U-Pb methods. Both samples were provided by the Irish Petroleum Affairs Division, Dublin.

The results presented here complement a larger confidential study of the igneous evolution of the UK Atlantic Margin undertaken by BGS and Rockall Consortium.

#### 1. Introduction

Six samples of igneous rocks from wells and boreholes from the Irish Shelf were examined with the intention of carrying out a programme of Ar-Ar geochronology. Unfortunately, suitable separates of fresh plagioclase feldspar were obtained from only one sample (from well 62/7-1). In addition, U-Pb/Pb-Pb isochron dating of one further sample (from well 13/3-1) was attempted.

## 2. Ar-Ar geochronology

#### 2.1 METHODOLOGY

Basalt samples recovered from well 62/7-1 were screened by petrographic examination. The samples were crushed and sieved and plagioclase feldspar was concentrated using magnetic separation and heavy fluid separation. Splits were leached in dilute HNO<sub>3</sub> to remove alteration products (e.g. clay) and pristine crystals of plagioclase were hand-picked using a binocular microscope for Ar-Ar dating. Two aliquots of plagioclase were prepared. Purified separates were loaded into Cu packets (packet 37 and 48), placed into a quartz vial and then loaded into an Al can for irradiation (EK54). Adjacent to both sample packets in the quartz vial we placed Al packets of the international standard Taylor Creek Rhyolite sanidine (TCR;  $28.34 \pm 0.16$  Ma, Renne *et al.*, 1998) to permit characterization of the irradiation flux to the samples. The samples were irradiated in the Petten HFR reactor for 48 hours in the Cd lined facility (RODEO).

Samples were step heated using a resistively heated double-vacuum furnace over a temperature range from 500 to 1600 °C. Samples were heated for 5 minutes prior to 10 minutes cleanup. Extracted gases were cleaned using 3 GP50 SAES getters (two operated at 450 °C and one at room temperature). Furnace blanks were stable at less than 1.2 x 10<sup>-14</sup> <sup>40</sup>Ar, 8.5 x 10<sup>-17</sup> mol <sup>39</sup>Ar, 6.8 x 10<sup>-17</sup> <sup>38</sup>Ar and <sup>37</sup>Ar, and 1.4 x 10<sup>-16</sup> <sup>36</sup>Ar. Data were collected using an ARGUS multicollector mass spectrometer at the NERC Argon Isotope Facility, SUERC. The ARGUS employs five high-gain, low-noise Faraday detectors with 10<sup>11</sup> (<sup>40</sup>Ar) and 10<sup>12</sup> (<sup>39-36</sup>Ar) ohm resistors for simultaneous collection of all five isotopes of Ar. The ARGUS has a sensitivity of 1.35 x 10<sup>-3</sup> A/Torr.

Ar-Ar Calc (Koppers 2002) was used to regress and reduce age data. Isotope data are corrected for blank, radioactive decay, mass discrimination and interfering reactions. Ar-Ar ages also include a 0.5% error assigned to the J-parameter. J values and interference correction factors are presented below tabulated data (Tables 1 and 2).

#### 2.2 DATA

Tables 1 and 2 summarise the geochronological Ar-Ar data and give age information for weighted plateaus (Figs. 1.1 and 1.3), total fusion ages and inverse isochron ages (Figs. 1.2 and 1.4). Inverse isochron plots are constructed using data which were included in the weighted plateau calculations for which the acceptance criteria are n=3 for minimum number of contiguous steps, F=0.60 (that is,  $\geq 60\%$  of <sup>39</sup>Ar released) and P=0.05 for the probability of fit. The weighted plateau ages, total fusion ages and inverse isochron ages are all concordant within  $2\sigma$  limits, and excess <sup>40</sup>Ar is not evident in either aliquot.

Given the high-degree of consistency between the Ar-Ar ages derived using different numerical techniques and the statistical testing of the data, we accept that the Ar-Ar ages are representative of crystallisation and not a secondary process such as re-heating or alteration. Our preferred age of  $93.8 \pm 1.0$  Ma is derived from the weighted mean of the two plateau ages.

Table 1. Ar isotope data for sample 62/7-1 (packet 37)

62/7-1 [packet 37], 15.12 mg plagioclase,  $J = 0.0133815 \pm 0.0000669$ , lab# 13004-13025

	Furnace power	Plateau steps	<sup>36</sup> Ar <sub>atm</sub> (√)	<sup>37</sup> Ar <sub>Ca</sub> (V)	<sup>38</sup> Ar <sub>CI</sub> (V)	<sup>39</sup> Ar <sub>K</sub> (V)	<sup>40</sup> Ar* (∨)	<sup>40</sup> Α <b>r*</b> / <sup>39</sup> Αr <sub>K</sub>	Age (Ma)	2σ (Ма)	<sup>40</sup> Ar* (%)	K/Ca	2σ
1	7.0 %		0.00175	0.00027	0.00063	0.00348	0.04430	12.73	284.36	146.40	7.89	5.45	5.45
2	7.5 %		0.00040	0.00046	0.00007	0.00762	0.04268	5.60	130.63	40.34	26.58	7.05	4.57
3	8.0 %		0.00046	0.00130	0.00001	0.01805	0.08864	4.91	115.12	18.79	39.40	5.99	1.18
4	9.0 %	1	0.00118	0.00555	0.00000	0.06573	0.27482	4.18	98.45	6.86	43.97	5.09	0.28
5	10.0 %	/	0.00119	0.00982	0.00000	0.11145	0.44930	4.03	95.01	4.25	56.12	4.88	0.20
6	11.0 %	/	0.00122	0.01055	0.00000	0.12142	0.48624	4.00	94.40	3.72	57.43	4.95	0.19
7	12.0 %	/	0.00104	0.00920	0.00000	0.10636	0.43044	4.05	95.37	4.00	58.36	4.97	0.23
8	13.0 %	/	0.00142	0.01184	0.00000	0.13541	0.53711	3.97	93.52	3.79	56.14	4.92	0.19
9	14.2 %	/	0.00134	0.01069	0.00000	0.12869	0.49986	3.88	91.63	3.74	55.88	5.18	0.22
10	15.5 %	/	0.00094	0.00836	0.00000	0.09437	0.37604	3.98	93.94	4.18	57.39	4.86	0.24
11	17.0 %	/	0.00077	0.00680	0.00000	0.07608	0.30115	3.96	93.33	4.74	57.03	4.81	0.27
12	19.0 %	1	0.00069	0.00545	0.00000	0.06393	0.24498	3.83	90.43	6.03	54.42	5.04	0.28
13	21.0 %	1	0.00084	0.00715	0.00000	0.08499	0.34822	4.10	96.52	4.48	58.45	5.11	0.26
14	24.0 %	1	0.00539	0.04693	0.00000	0.56049	2.30876	4.12	97.03	2.79	59.18	5.14	0.17
15	25.0 %	1	0.00253	0.02208	0.00000	0.25734	1.04020	4.04	95.26	3.06	58.16	5.01	0.17
16	26.0 %	1	0.00170	0.01506	0.00000	0.16759	0.66004	3.94	92.87	3.74	56.75	4.78	0.19
17	27.5 %	1	0.00114	0.00969	0.00000	0.11523	0.46694	4.05	95.49	3.79	58.13	5.11	0.24
18	29.5 %	1	0.00074	0.00616	0.00000	0.06830	0.26677	3.91	92.12	5.24	54.89	4.77	0.29
19	32.0 %	1	0.00053	0.00428	0.00000	0.04452	0.17180	3.86	91.04	7.99	52.50	4.48	0.35
20	35.0 %	1	0.00040	0.00307	0.00000	0.03658	0.14341	3.92	92.46	9.15	54.82	5.13	0.50
21	40.0 %		0.00019	0.00141	0.00003	0.01151	0.03155	2.74	65.13	27.47	35.58	3.51	0.83
22	50.0 %		0.00014	0.00056	0.00001	0.00614	0.01262	2.06	49.11	56.16	23.23	4.74	2.45
		Σ	0.02599	0.19670	0.00076	2.28529	9.22589						
		<sup>40</sup> Ar*/ <sup>39</sup> Ar <sub>K</sub>	2σ	<sup>40</sup> Ar/ <sup>36</sup> Ar	2σ	Age (Ma)	2σ (Ma)	MSWD	<sup>39</sup> Ar <sub>K</sub> (%,n)	K/Ca	2σ		
Weighted pla	ateau	4.01	± 0.04	-	-	94.48	1.37 ± 1.45%	0.84	97.95% 17	4.97	0.07		
Total fusion a	age	4.04	± 0.05			95.14	1.46 ± 1.53%		- 22	4.96	0.08		
nverse isoch	hron	3.85	± 0.37	310.63	± 38.14	90.91	8.58 ± 9.43%	0.85					

NOTE: Isotope data corrected for blank, radioactive decay, mass discrimination and interferring reactions  $(^{40}\text{Ar}/^{99}\text{Ar})_{\text{K}} = 0.001830 \pm 0.000092$ ,  $(^{30}\text{Ar}/^{97}\text{Ar})_{\text{Ca}} = 0.000699 \pm 0.000035$ ,  $(^{36}\text{Ar}/^{97}\text{Ar})_{\text{Ca}} = 0.000270 \pm 0.000014$  Ages include 0.5% error assigned to J-parameter

Table 2. Ar isotope data for sample 62/7-1 (packet 48)

62/7-1 [packet 48], 13.67 mg plagioclase, J = 0.0133377  $\pm$  0.0000667, lab#13029-13052

	Furnace power	Plateau steps	<sup>36</sup> Ar <sub>atm</sub> (√)	<sup>37</sup> Ar <sub>Ca</sub> (V)	<sup>38</sup> Ar <sub>CI</sub> (V)	<sup>39</sup> Ar <sub>K</sub> (√)	<sup>40</sup> Ar* (∨)	<sup>40</sup> Α <b>r*</b> / <sup>β9</sup> Αr <sub>K</sub>	Age (Ma)	2σ (Ма)	<sup>40</sup> Ar* (%)	K/Ca	2σ
1	7.0 %		0.00126	0.00045	0.00034	0.00453	0.02830	6.25	144.83	± 86.80	7.05	4.35	2.61
2	7.5 %		0.00049	0.00078	0.00004	0.00880	0.04276	4.86	113.58	± 30.07	22.97	4.85	1.65
3	8.0 %		0.00056	0.00221	0.00004	0.02215	0.07759	3.50	82.57	± 13.87	31.98	4.32	0.48
4	9.0 %	/	0.00106	0.00690	0.00000	0.07756	0.30627	3.95	92.81	± 4.83	49.47	4.83	0.22
5	10.0 %	/	0.00127	0.01062	0.00000	0.12025	0.46713	3.88	91.35	± 3.49	55.42	4.87	0.17
6	11.0 %	/	0.00141	0.01232	0.00000	0.13785	0.53141	3.86	90.67	± 3.37	56.05	4.81	0.18
7	12.0 %	/	0.00137	0.01195	0.00000	0.13239	0.51751	3.91	91.90	± 3.18	56.14	4.76	0.18
8	13.0 %	/	0.00137	0.01111	0.00000	0.12824	0.50038	3.90	91.74	± 4.00	55.18	4.96	0.20
9	14.2 %	/	0.00121	0.01055	0.00000	0.11390	0.44932	3.95	92.73	± 3.44	55.64	4.64	0.18
10	15.5 %	/	0.00088	0.00775	0.00000	0.08654	0.32650	3.77	88.78	± 3.67	55.77	4.80	0.18
11	17.0 %	/	0.00078	0.00710	0.00000	0.07821	0.30302	3.87	91.11	± 3.85	56.73	4.74	0.23
12	19.0 %	1	0.00064	0.00636	0.00000	0.06624	0.25942	3.92	92.07	± 4.08	57.87	4.48	0.20
13	21.0 %	1	0.00094	0.00799	0.00000	0.09241	0.36474	3.95	92.77	± 3.56	56.78	4.98	0.20
14	22.0 %	1	0.00147	0.01349	0.00000	0.15679	0.64490	4.11	96.58	± 3.04	59.76	5.00	0.18
15	23.0 %	1	0.00222	0.01949	0.00000	0.22988	0.93223	4.06	95.26	± 2.90	58.65	5.07	0.17
16	24.0 %	1	0.00218	0.01965	0.00000	0.22910	0.94210	4.11	96.56	± 2.93	59.41	5.01	0.16
17	25.0 %	1	0.00155	0.01341	0.00000	0.15341	0.59839	3.90	91.71	± 3.22	56.60	4.92	0.17
18	26.0 %	1	0.00186	0.01611	0.00000	0.18505	0.73013	3.95	92.74	± 3.11	57.03	4.94	0.18
19	27.5 %	1	0.00113	0.01000	0.00000	0.11615	0.47184	4.06	95.41	± 3.27	58.48	5.00	0.20
20	29.5 %	1	0.00044	0.00384	0.00000	0.04279	0.16792	3.92	92.25	± 5.98	56.51	4.79	0.27
21	32.0 %	1	0.00042	0.00425	0.00000	0.04331	0.17780	4.11	96.40	± 6.25	58.78	4.38	0.32
22	35.0 %		0.00017	0.00190	0.00004	0.01832	0.07811	4.26	100.01	± 12.18	61.07	4.14	0.44
23	40.0 %		0.00015	0.00130	0.00000	0.01237	0.04187	3.38	79.83	± 18.33	49.04	4.10	0.75
24	50.0 %		0.00015	0.00151	0.00000	0.01324	0.05690	4.30	100.77	± 17.76	56.55	3.76	0.65
		Σ	0.02497	0.20105	0.00046	2.26949	9.01655						
		<sup>40</sup> Ar*/ <sup>39</sup> Ar <sub>K</sub>	2σ	<sup>40</sup> Ar/ <sup>36</sup> Ar	2σ	Age	2σ	MSWD	<sup>39</sup> Ar <sub>K</sub>	K/Ca	2σ		
		OI / OIK	20	AI/ AI	20	(Ma)	(Ma,%)		(%,n)				
Veighted Pl	lateau	3.96	± 0.05	-		93.09	1.41 ± 1.51%	1.65	96.50% 18	4.86	0.08		
otal Fusion	ı Age	3.97	± 0.04	-		93.37	1.26 ± 1.35%		- 24.00	4.84	0.09		
verse isoc	hron	3.99	± 0.57	292.60	± 71.12	93.77	13.09 ± 13.96%	1.76	-		-		

NOTE: Isotope data corrected for blank, radioactive decay, mass discrimination and interferring reactions ( $^{40}$ Ar/ $^{39}$ Ar)<sub>K</sub> = 0.001830  $\pm$  0.000092, ( $^{39}$ Ar/ $^{37}$ Ar)<sub>Ca</sub> = 0.000699  $\pm$  0.000035, ( $^{36}$ Ar/ $^{37}$ Ar)<sub>Ca</sub> = 0.000270  $\pm$  0.000014 Ages include 0.5% error assigned to J-parameter

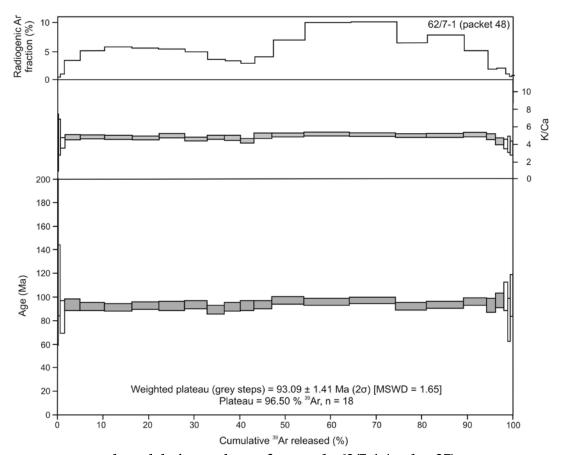


Figure 1.3 released during each step for sample 62/7-1 (packet 37). Ar-Ar age spectrum, K/Ca ratios and percentage of radiogenic <sup>40</sup>Ar released during each step for sample 62/7-1 (packet 48).

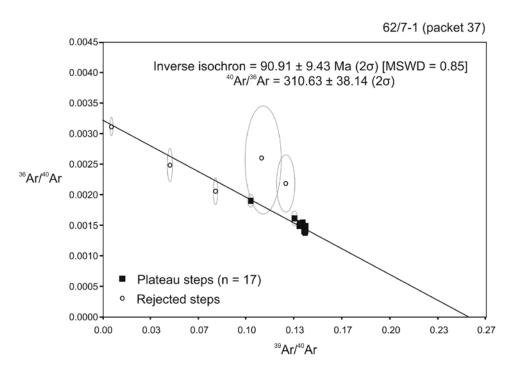


Figure 1.2 Inverse isochron plot constructed using accepted steps from age spectrum for sample 62/7-1 (packet 37).

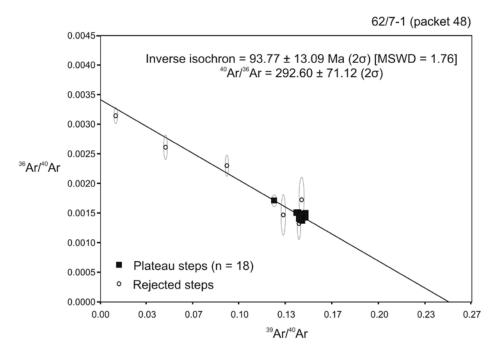


Figure 1.4 Inverse isochron plot constructed using accepted steps from age spectrum for sample 62/7-1 (packet 48).

## 3. U-Pb geochronology

A sample of basalt from well 13/3-1 did not contain suitable feldspar crystals for Ar-Ar dating. It was therefore decided to attempt to derive U-Pb and/or Pb-Pb isochron ages using separates of pyrite and apatite. This approach relies on the fact that apatite may have elevated U/Pb ratios, leading to the formation of radiogenic lead, whereas pyrite has very low U/Pb.

Pyrite and apatite crystals were concentrated using heavy liquids and magnetic separation. Pure separates were hand-picked using a binocular microscope. After washing with MilliQ water in an ultrasonic bath, the samples were spiked with an enriched <sup>205</sup>Pb-<sup>235</sup>U tracer, and dissolved in nitric acid. U and Pb were separated using standard anion-exchange techniques, and analysed on a Thermo Scientific Triton thermal ionisation mass spectrometer. Results are shown in Table 3. Unfortunately, the range in U/Pb and Pb-isotope ratios was not sufficient to allow calculation of a meaningful age.

Table 3. U-Pb data for pyrite and apatite separates from 13/3-1.

	<sup>238</sup> U/ <sup>204</sup> Pb	% err	<sup>206</sup> Pb <sup>/204</sup> Pb	% err	$\rho_{8/4-6/4}$	<sup>235</sup> U/ <sup>204</sup> Pb	% err	<sup>207</sup> Pb <sup>/204</sup> Pb	% err	$\rho_{5/4-7/4}$
Pyrite	0.4516	0.16	17.947	0.14	0.34	0.00327	0.16	15.509	0.23	0.39
Apatite	253.4	1.23	24.099	1.22	0.99	1.838	1.23	15.898	1.23	0.97

#### 4. Discussion

Basalts from 62/7-1 have previously been described by Tate & Dobson (1988), who reported K-Ar ages of c. 85 and 133.5 Ma. On the basis that the lavas are extrusive, and are overlain by a

thick Cretaceous section, Tate & Dobson considered that the c. 85 Ma age must be invalid, and preferred the c. 133.5 Ma age. The Ar-Ar age reported here (93.8  $\pm$  1.0 Ma) is closer to the younger K-Ar age and this has potential implications for the age of the overlying Cretaceous sediments.

### References

British Geological Survey holds most of the references listed below, and copies may be obtained via the library service subject to copyright legislation (contact libuser@bgs.ac.uk for details). The library catalogue is available at: <a href="http://geolib.bgs.ac.uk">http://geolib.bgs.ac.uk</a>.

KOPPERS, A.A.P., 2002. ArArCALC - software for Ar-40/Ar-39 age calculations. *Computers and Geosciences*, **28**, 605-619.

RENNE, P., KARNER, B. & LUDWIG, K.R., 1998. Radioisotope dating - Absolute ages aren't exactly. *Science*, **282**, 1840-1841.

TATE, M.P. & DOBSON, M.R. 1988. Syn- and post-rift igneous activity in the Porcupine Seabight Basin and adjacent continental margin W of Ireland. *In:* Morton, A.C. & Parson, L.M. (eds), *Early Tertiary Volcanism and the Opening of the NE Atlantic*. Geological Society of London Special Publication, **39**, 309-344.