

A re-appraisal of the petrogenesis and tectonic setting of the Ordovician Fishguard Volcanic Group, SW Wales

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Abstract – The Fishguard Volcanic Group represents an excellently preserved example of a volcanic sequence linked to the closure of the Iapetus Ocean. This study re-examines the petrogenesis and proposed tectonic setting for the Llanvirn (467–458 Ma) Fishguard Volcanic Group, South Wales, UK. New major and trace element geochemical data and petrographic observations are used to re-evaluate the magma chamber processes, mantle melting and source region. The new data reveal that the Fishguard Volcanic Group represents a closely related series of basalts, basaltic andesites, dacites and rhyolites originating from a spinel lherzolite source which had been modified by subduction components. The rocks of the Fishguard Volcanic Group are co-genetic and the felsic members are related to the more primitive basalts mainly by low-pressure fractional crystallization. The geochemistry of the lavas was significantly influenced by subduction processes associated with a coeval arc, while significant amounts of assimilation of continental crust along with fractional crystallization appear to have contributed to the compositions of the most evolved lavas. The Fishguard Volcanic Group was erupted into a back-arc basin where extensive rifting but no true seafloor spreading had occurred.

Keywords: geochemistry, magmatism, back-arc basin, subduction.

1. Introduction

The closure of the Iapetus Ocean (510–410 Ma) was one of the most significant events in the geological evolution of northwestern Europe (e.g. Trench & Torsvik, 1992; Cocks & Torsvik, 2006, 2011; Murphy & Nance, 2008; van Staal *et al.* 2009). However, our understanding of the tectonomagmatic development, both of this ocean and of the marginal subduction zones along which Iapetus oceanic crust was ultimately consumed, is restricted to somewhat limited exposures. The igneous rocks of the Fishguard Volcanic Group in SW Wales represent an excellently preserved example of rocks associated with the closure of the Iapetus Ocean.

During the emplacement of the Fishguard Volcanic Group in early–middle Ordovician time (485–458 Ma), Wales formed part of the southern margin of the closing Iapetus Ocean. Avalonia (the microcontinent of which Wales was a part) moved northward from 55° S to 30° S in the period from the Arenig (478–467 Ma) to the Ashgill (451–444 Ma) (Fitton, Thirlwall & Hughes, 1982). During this period a number of island arc chains and marginal basins formed above the southeastward-dipping subduction zone on the north side of Avalonia along a NE-trending plate margin (Fitton & Hughes 1970; Phillips, Stillman & Murphy, 1976; Fitton, Thirlwall & Hughes, 1982; Murphy & Nance, 2008; Murphy, Hamilton & LeBlanc, 2011). Ordovician sequences of both basic and/or silicic lavas are present not only in the Fishguard region but throughout

Wales, in areas such as Snowdonia and Ramsey Island (Fig. 1) (Kokelaar *et al.* 1984b).

A re-evaluation of the Fishguard Volcanic Group is required as earlier studies were based on a limited range of geochemical elements. Furthermore, previous geochemical investigations have shown that the rocks are similar in composition to present-day mid-ocean ridge basalt (MORB), while also displaying a relative depletion in Nb (Bevins, 1982). However, the use of tungsten carbide crushing mills in these earlier studies may have affected the Nb concentration of the rocks (e.g. Hickson & Juras, 1986) and so to avoid this problem this study has used agate crushing mills. This study presents new major and trace element geochemical data and petrographic observations to re-evaluate the petrogenesis and tectonic setting of the Llanvirn-age (467–458 Ma) Fishguard Volcanic Group.

2. Local geology and previous work

Most of the Ordovician volcanism in west Wales occurred in the period from the Arenig to the Llanvirn (478–458 Ma) (Thomas & Thomas, 1956; Bevins & Roach, 1979). The overall consensus is that the Ordovician rocks of Wales were emplaced in a supra-subduction back-arc basin, in a mostly submarine environment on immature continental crust on the southeast side of the Iapetus Ocean (Bevins, 1982; Bevins, Kokelaar & Dunkley, 1984; Kokelaar *et al.* 1984b; Leat *et al.* 1986). All of the Lower Palaeozoic rocks in Wales and the Welsh Borderland were affected by low-grade

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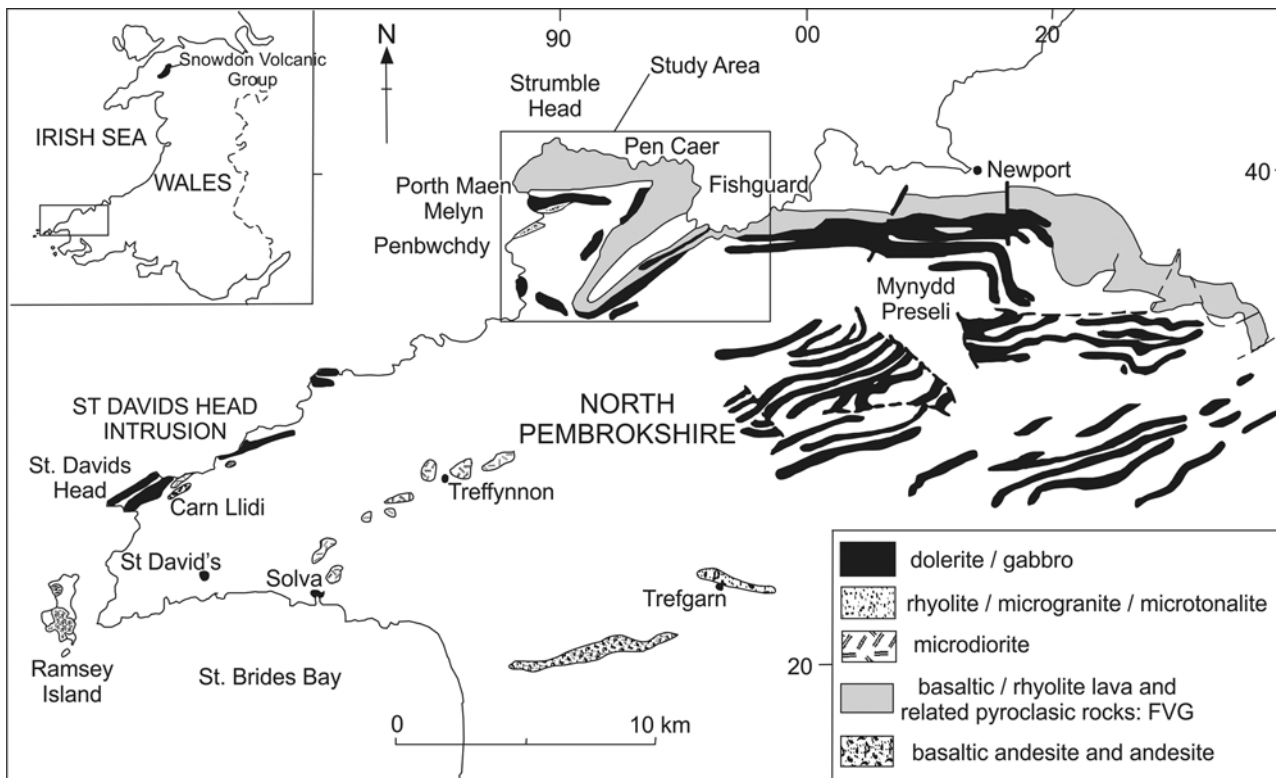


Figure 1. Map adapted from Bevins *et al.* (1991) showing the location of the Ordovician igneous rocks of north Pembrokeshire and the rest of Wales in relation to one another. The rock types of the study area are also shown.

(zeolite to low-grade greenschist facies) metamorphism, primarily due to burial (Bevins & Rowbotham, 1983; Bevins & Robinson, 1988; Robinson *et al.* 1999).

Early work on the geology of the area was reported by Reed (1895), Cox (1930) and Thomas & Thomas (1956). The Fishguard Volcanic Group (Reed, 1895; Thomas & Thomas, 1956; R. E. Bevins, unpub. Ph.D. thesis, Univ. Keele, 1979; Bevins, 1982; Bevins, Kokelaar & Dunkley, 1984; Kokelaar *et al.* 1984b; Leat *et al.* 1986; Bevins, Lees & Roach, 1991) is located in the Strumble Head to Fishguard area of north Pembrokeshire, Wales (Fig. 1), close to the older Trefgarn basaltic andesite to andesite lavas of Tremadoc age (485–478 Ma), which are thought to represent the products of a volcanic arc (Bevins, Kokelaar & Dunkley, 1984).

Fishguard Volcanic Group samples were collected from an area around the Strumble Head Peninsula (Figs 1, 2). The volcanic group comprises three formations, from oldest to youngest: (1) the predominantly rhyodacitic to rhyolitic Porth Maen Melyn Volcanic Formation; (2) the pillowed basalts of the Strumble Head Volcanic Formation; and (3) the rhyolitic Goodwick Volcanic Formation (Bevins, 1982) (Fig. 2).

The Porth Maen Melyn Volcanic Formation (Bevins & Roach, 1979) is composed principally of rhyolitic tuffs, ash flow tuffs, rhyolite lavas, autobreccias, debris flow breccias and, to a lesser extent, massive and pillowed rhyodacite lavas. Small volumes of intermediate magmas were also emplaced as microtonalite intrusions (Bevins & Roach, 1979).

Conformably overlying this formation is the Strumble Head Volcanic Formation. Basaltic pillow lavas with well-developed inter-pillow breccias, local elongate steeply inclined lava tubes and necking structures are found at the contact with the Porth Maen Melyn Volcanic Formation (Bevins, 1982). The formation also comprises massive lensoid lava sheets, thin hyaloclastites, basaltic tuffs, rare rhyolitic tuff horizons and high-level intrusive basaltic sheets (Bevins & Roach, 1979). The boundary between this formation and the overlying rhyolitic Goodwick Volcanic Formation is marked by a complex interdigitation of lavas and high-level intrusions (Kokelaar *et al.* 1984a).

The Goodwick Volcanic Formation progresses stratigraphically upwards through thick rhyolitic domes and flows to autobrecciated rhyolites and fine tuffaceous silicic rocks which are intruded by a thick basic sill. The sill is bulbous at the base and pillowed at the top indicative of having been intruded into wet sediment (Kokelaar *et al.* 1984a).

The volcanic group is composed of up to 1.8 km of volcanic and intrusive rocks, deposited in a locally subsiding basin (Kokelaar *et al.* 1984a, b). The rocks were extruded in a mostly submarine environment with restricted occurrences of subaerial volcanism (Bevins, 1982; Kokelaar *et al.* 1984a, b; Kokelaar, 1988). Sediment gravity flow deposits are found interstratified with the pillow lavas, although these are not derived from the lavas and so no topographic highs are thought to have developed (Kokelaar *et al.* 1984a, b; Kokelaar, 1988).

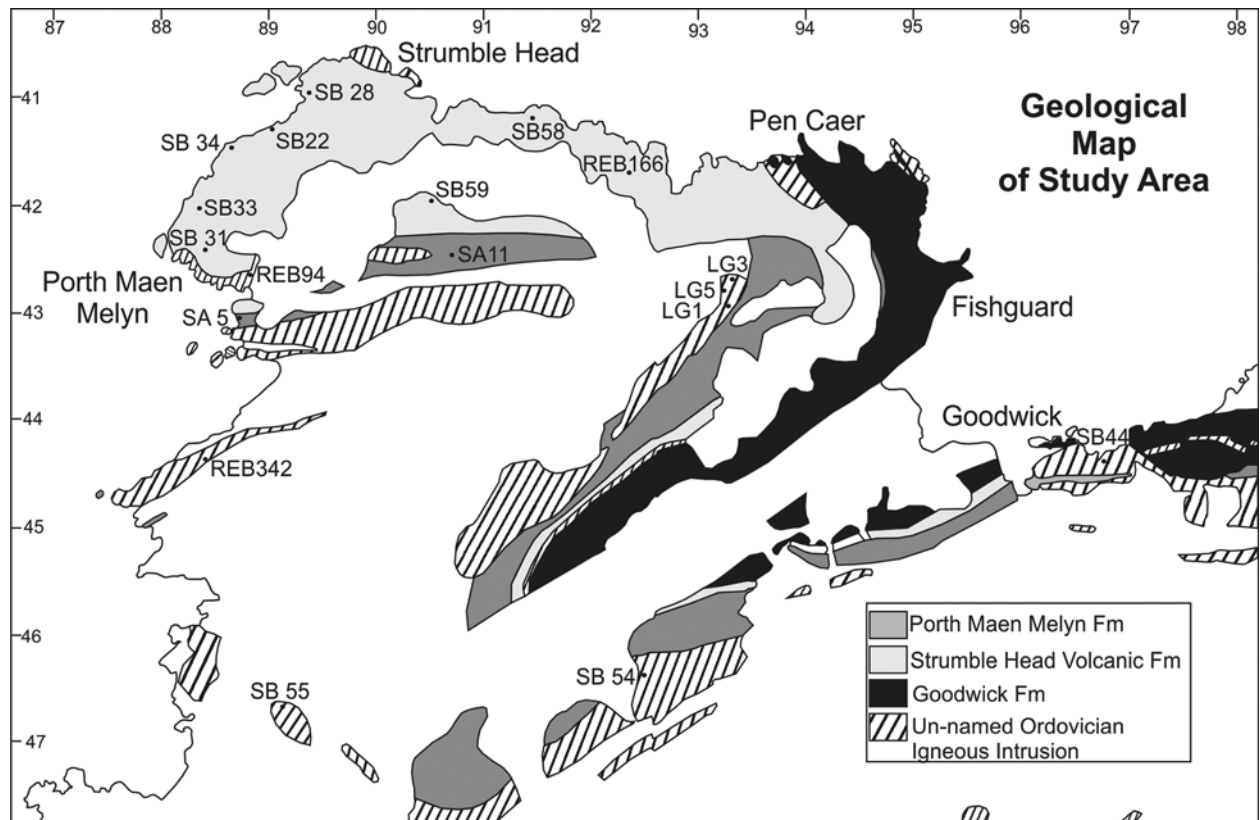


Figure 2. Geological map showing the locations of the samples analysed in this study. Also highlighted are the formations that have been sampled. The non-patterned portion of the map represents unrelated rocks and Quaternary cover.

The basaltic and intermediate lavas and intrusions were recognized as tholeiitic by Bevins (1982) and were proposed to be derived by low-pressure fractional crystallization of a parental magma that originated in the upper mantle. Bevins, Lees & Roach (1991) noted that some of the silicic intrusive and extrusive rocks display a calc-alkaline trend as opposed to a tholeiitic trend. It is uncertain whether the dacite and rhyolite magmas were derived from the same source as the basaltic rocks, although limited trace element data for the rhyolites reported by Bevins, Lees & Roach (1991) are consistent with such an origin.

3. Petrography

Eighteen basic, intermediate and silicic rocks from the samples collected by R. E. Bevins (unpub. Ph.D. thesis, Univ. Keele, 1979) were re-examined petrographically (online Supplementary Material Table S1 available at <http://journals.cambridge.org/geo>). Basalt sample SB34 is from a pillow lava and contains tabular clinopyroxene, minor plagioclase, secondary chlorite and pumpellyite. Other pillowed basalts (samples SB31 and SB58) contain zoned clinopyroxene and plagioclase as microphenocrysts in a groundmass of spherulitic (quenched) clinopyroxene and plagioclase. Sample SB33 consists of tabular plagioclase and interstitial clinopyroxene with secondary chlorite and comes from a massive basaltic lava. The basaltic intrusions (samples LG3, LG1 and LG5) contain euhed-

ral, subophitic clinopyroxene, altered tabular plagioclase, abundant chlorite and, in the case of LG5, epidote. Other intrusive basaltic sheets (samples REB166, SB22, SB44, SB28 and SB59) contain albitized plagioclase with subophitic clinopyroxene and chlorite. Samples SB54 and SB55 are also from intrusive basaltic sheets; however, they comprise clinopyroxene and plagioclase phenocrysts set in a finer feldspathic groundmass along with Fe–Ti oxides. The rhyolitic flow samples (SA11 and SA5) are fine grained with quartz-feldspar groundmass (most likely recrystallized from glass) and also contain quartz and epidote veins. Both the rhyodacite lava (sample REB94) and the microtonalite intrusion (sample REB342) contain plagioclase, quartz, chlorite and rare biotite. The field relations of these samples are discussed in detail in Bevins (1982).

4. Analytical techniques

Eighteen samples (2 rhyolites, 2 dacites and 14 basalts) from the original sample set described and collected by R. E. Bevins (unpub. Ph.D. thesis, Univ. Keele, 1979) from a transect through the Fishguard Volcanic Group (Fig. 2 and online Supplementary Material Table S1 available at <http://journals.cambridge.org/geo>) were re-prepared and re-analysed for major and trace elements.

Following removal of weathered surfaces, the samples were crushed in a steel jaw crusher and powdered using an agate Tema mill at Cardiff University. Major and trace element abundances were analysed

using a JY Horiba Ultima 2 inductively coupled plasma optical emission spectrometer (ICP-OES) and a Thermo X7 series inductively coupled plasma mass spectrometer (ICP-MS) at Cardiff University, Wales. Further information regarding methods and instruments are discussed in McDonald & Viljoen (2006).

Accuracy and precision of the data were assessed using the international reference materials NIM-G and JB-1A (online Supplementary Material Table S2 available at <http://journals.cambridge.org/geo>). Relative standard deviations show accuracy of 1–5% for most major and trace elements for the standard materials used. Duplicate standard deviations are also within error, ensuring precision. A representative dataset can be found in Table 1 and the full dataset in the online Supplementary Material Table S3 available at <http://journals.cambridge.org/geo>.

5. Geochemical results

5.a. Element mobility

The rocks analysed in this study have all undergone low-grade sub-greenschist facies metamorphism (Bevins & Rowbotham, 1983; Robinson & Bevins, 1986) and this is reflected in the abundance of chlorite observed in the thin-sections along with less common pumpellyite, prehnite and epidote. Varying degrees of albitization have affected the rocks and so the concentrations of Al, Ca and Na in particular have been modified (Bevins, 1982). Under such metamorphic conditions many elements, in particular the large-ion lithophile elements, become mobile. Accordingly, these elements are not representative of the original magmatic composition of the rocks and so cannot be used to assess the petrogenetic processes that the magmas have undergone. In this study, therefore, we will use trace elements generally regarded to be relatively immobile during low-grade metamorphism, i.e. HFSE (high-field-strength elements) and REE (rare earth elements) (e.g. Pearce & Cann, 1973; Wood, Joron & Treuil, 1979; Merriman, Bevins & Ball, 1986).

5.b. Classification

A range of rock types is evident in the samples analysed, including basalts, basaltic andesites, dacites and rhyolites (Fig. 3a–c). In Figure 3a the basalts and dacites (with the exception of SB33) predominantly classify as tholeiitic, while the rhyolites are more calc-alkaline. However, silica contents are susceptible to mobility during sub-solidus hydrothermal alteration, and so several classification diagrams that are based on relatively immobile elements have also been used, i.e. the Zr/Ti v. Nb/Y and Th v. Co diagrams (Fig. 3b, c).

In Figure 3b the samples all plot in the subalkaline field as a continuum from basalt to rhyolite, and on this diagram two of the samples (SB59 and SB58) classify as basaltic andesite. On the Th–Co diagram (Fig. 3c) the majority of the samples plot in the calc-alkaline

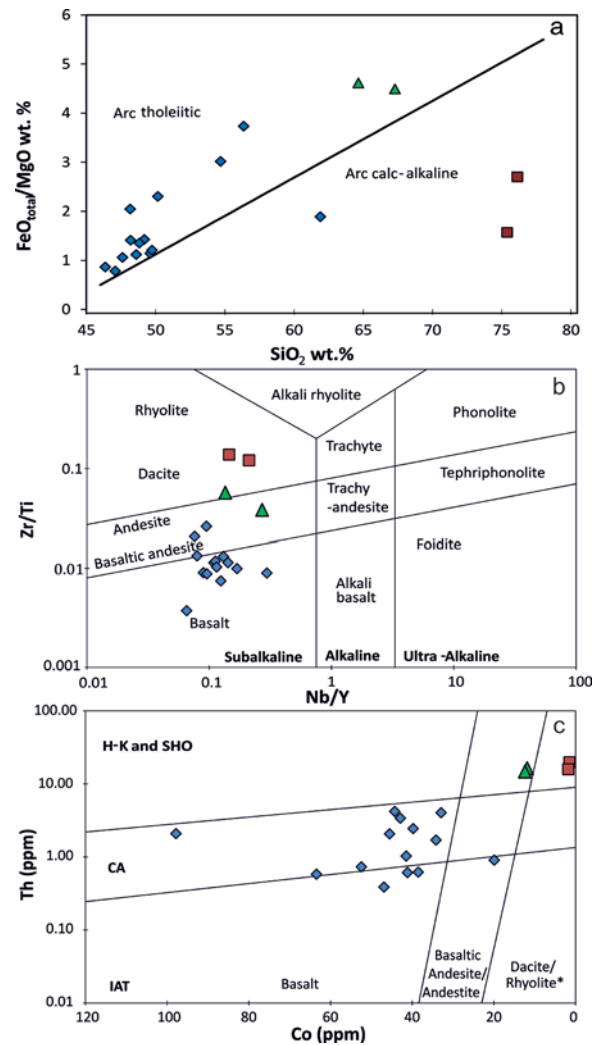


Figure 3. (Colour online) (a) Miyashiro (1975) basalt classification diagram showing the compositions of the studied samples. (b) Zr/Ti–Nb/Y classification diagram adapted from Pearce (2008). (c) Th–Co discrimination diagram (Hastie *et al.* 2007). Compositional fields: IAT – island arc tholeiite; CA – calc-alkaline; H-K – high-K calc-alkaline; SHO – shoshonite (* latites and trachytes also plot in the D/R fields).

field, with four of the basalts falling in the island arc tholeiite field. While the majority of basalts plot close to the dividing line between basalt and basaltic andesite, only sample SB55 plots in the basaltic andesite field. The rhyolites plot in the dacite/rhyolite field while the dacites fall on the andesite side of the boundary between andesite and dacite. The most evolved basalts appear to be samples SB59 and SB55, although the classification diagrams are generally inconclusive in this regard. Overall, the basalts and dacites of the group show a tholeiitic to tholeiitic/calc-alkaline transitional trend while the rhyolites have a more calc-alkaline type chemistry.

5.c. Basalt geochemistry

The basalts show an overall trend of increasing SiO_2 with decreasing MgO and increasing TiO_2 , K_2O , CaO

Table 1. Major and trace element data for the Fishguard Volcanic Group

Sample:	LG3	LG1	LG5	REB166	SB22	SB59	SB54	SB34	SB28
Major elements (wt%)									
SiO ₂	48.61	49.63	49.19	46.37	48.17	49.74	54.70	48.83	47.61
TiO ₂	1.40	1.38	1.75	1.44	2.14	1.16	2.47	1.26	1.67
Al ₂ O ₃	14.57	13.50	12.94	15.45	13.95	14.92	11.79	13.96	15.15
MnO	0.20	0.18	0.23	0.17	0.19	0.17	0.24	0.15	0.16
MgO	9.09	7.97	8.12	10.75	5.58	4.98	4.15	6.65	8.13
CaO	9.03	10.60	10.28	8.70	13.29	12.04	5.47	16.42	9.73
Na ₂ O	3.55	3.52	2.81	2.35	2.12	3.69	4.41	0.66	3.46
K ₂ O	0.60	0.37	0.47	0.75	0.45	0.25	0.10	0.02	0.99
P ₂ O ₅	0.13	0.14	0.19	0.13	0.29	0.17	0.31	0.13	0.21
FeO*	10.17	9.09	11.58	9.28	11.42	6.02	12.52	8.99	8.60
LOI	2.55	2.52	2.16	3.94	2.09	7.00	2.18	3.38	3.80
Total	99.90	98.90	99.72	99.33	99.69	100.14	98.34	100.45	99.51
Trace elements (ppm)									
Be	0.6	0.6	1.7	0.7	1.0	1.0	1.7	0.6	0.6
Sc	42	50	48	39	39	33	35	39	38
V	265	278	338	256	354	183	336	251	306
Cr	273	67	91	361	106	132	6	322	333
Co	46	41	98	47	42	43	35	39	64
Ni	24	18	13	52	23	49	16	29	87
Cu	126	105	106	79	84	87	82	133	70
Zn	55	19	49	47	46	32	81	23	64
Ga	18.8	19.2	44.0	21.4	25.4	25.4	24.5	26.6	23.0
Rb	13.3	6.8	22.2	10.2	5.8	4.5	1.8	0.2	20.7
Sr	244	293	200	259	490	85	106	363	239
Y	33.0	34.8	89.0	31.3	51.7	64.6	63.3	31.3	43.2
Zr	88.6	95.6	120.8	78.6	136.5	184.8	196.4	69.2	89.5
Nb	5.25	3.76	9.70	9.14	5.82	6.04	8.17	2.77	4.04
Mo	0.32	0.14	0.59	0.14	1.72	0.10	0.13	0.41	0.25
Sn	1.88	1.62	2.64	1.83	0.52	0.67	0.82	0.44	0.54
Cs	1.56	0.85	0.88	1.39	0.46	0.34	2.22	0.30	1.07
Ba	114	81	157	134	160	71	226	7	52
La	6.72	6.12	14.60	5.71	9.44	14.76	18.47	5.59	6.89
Ce	17.38	16.60	40.66	15.07	25.56	37.72	45.39	14.77	19.35
Pr	2.69	2.64	6.59	2.42	3.94	5.35	6.35	2.23	3.06
Nd	13.15	13.10	33.25	12.23	19.95	25.30	29.58	11.12	15.88
Sm	4.14	4.15	10.62	3.83	6.02	7.13	8.11	3.55	5.12
Eu	1.34	1.40	3.37	1.47	2.05	1.77	2.38	1.21	1.81
Gd	4.22	4.54	11.32	4.06	7.14	8.20	9.06	4.12	5.86
Tb	0.81	0.86	2.18	0.79	1.27	1.49	1.57	0.76	1.06
Dy	5.33	5.62	13.93	5.11	8.08	9.49	9.84	4.88	6.79
Ho	1.03	1.13	2.75	1.02	1.52	1.84	1.87	0.93	1.26
Er	2.96	3.14	7.94	2.93	4.41	5.56	5.42	2.70	3.62
Tm	0.46	0.49	1.21	0.45	0.73	0.93	0.88	0.45	0.59
Yb	2.96	3.10	7.84	2.95	4.57	6.09	5.61	2.87	3.70
Lu	0.46	0.47	1.19	0.46	0.66	0.88	0.82	0.39	0.53
Hf	2.88	2.91	3.61	2.75	4.35	6.38	5.83	2.49	3.02
Ta	0.38	0.28	0.62	0.62	0.40	0.36	0.56	0.18	0.23
Th	2.14	0.71	2.15	0.40	1.05	3.46	4.04	0.72	0.60
U	0.31	0.28	0.62	0.17	0.34	0.94	1.07	0.27	1.10
Sample:	SB31	SB58	SB33	SB55	SB44	SA5	SA11	REB342	REB94
Major elements (wt%)									
SiO ₂	50.16	48.20	61.90	56.37	43.95	76.13	75.40	64.65	67.29
TiO ₂	2.78	1.27	1.86	1.84	3.54	0.23	0.15	0.95	1.08
Al ₂ O ₃	12.29	12.87	11.79	15.26	10.74	12.00	11.64	14.73	14.28
MnO	0.22	0.15	0.16	0.21	0.28	0.04	0.02	0.16	0.15
MgO	5.80	5.40	4.12	2.50	7.00	0.78	0.67	1.41	1.38
CaO	8.20	11.95	4.87	5.19	9.82	0.35	0.003	0.55	2.80
Na ₂ O	3.30	4.24	4.41	6.76	2.26	3.44	2.18	3.55	3.48
K ₂ O	0.86	0.25	0.68	0.07	0.52	4.79	6.13	3.28	1.26
P ₂ O ₅	0.29	0.32	0.21	0.52	0.40	0.05	0.01	0.24	0.26
FeO*	13.36	7.61	7.80	9.32	17.75	2.10	1.05	6.51	6.19
LOI	2.02	7.96	1.69	1.41	2.35	0.74	0.66	2.39	1.93
Total	99.28	100.22	99.49	99.45	98.61	100.65	97.91	98.42	100.10
Trace elements (ppm)									
Be	1.3	1.3	1.2	1.3	0.9	2.1	2.1	2.8	2.9
Sc	41	29	41	22	57	4	3	22	23
V	440	179	325	98	854	10	1	96	129
Cr	19	122	100	10	48	24	11	23	29
Co	44	40	36	20	53	1	1	12	11

Table 1. Continued

Sample:	SB31	SB58	SB33	SB55	SB44	SA5	SA11	REB342	REB94
Ni	5	27	15	2	50	2	4	3	3
Cu	40	64	20	40	100	31	12	34	39
Zn	66	37	51	43	59	56	16	23	45
Ga	23.1	23.6	17.7	26.9	24.5	19.5	19.3	26.8	27.3
Rb	15.3	3.7	10.9	1.3	7.9	84.4	182.2	105.1	55.0
Sr	200	133	163	242	193	56	38	101	303
Y	56.4	81.5	35.7	76.3	47.9	62.3	56.6	59.2	62.0
Zr	127	160	132	151	76	175	126	315	266
Nb	6.90	6.12	4.94	5.96	3.25	12.59	8.55	8.17	16.05
Mo	0.32	1.46	0.14	0.24	0.26	1.61	0.64	0.51	0.66
Sn	0.60	0.72	0.63	0.57	0.50	3.40	0.73	0.54	0.98
Cs	0.61	0.92	0.50	0.64	0.83	0.82	0.91	2.25	1.89
Ba	278	171	191	45	147	752	493	931	594
La	16.65	15.68	10.71	13.02	8.79	34.85	26.87	38.65	43.38
Ce	40.01	38.52	26.49	36.32	23.74	75.13	59.46	85.33	93.95
Pr	5.55	5.54	3.74	5.72	3.66	9.45	7.94	10.34	11.37
Nd	25.96	27.07	17.76	29.20	19.22	36.66	33.95	41.80	47.02
Sm	7.23	7.77	4.98	8.86	5.87	8.65	8.48	9.10	10.18
Eu	2.23	2.02	1.61	3.11	1.99	1.13	1.02	2.17	2.12
Gd	7.94	9.05	5.56	10.33	6.78	7.95	8.47	9.29	10.31
Tb	1.41	1.65	0.96	1.84	1.19	1.46	1.48	1.53	1.63
Dy	8.69	11.01	5.93	11.70	7.56	9.27	9.18	9.11	9.63
Ho	1.65	2.19	1.10	2.26	1.43	1.85	1.73	1.71	1.76
Er	4.81	6.76	3.12	6.59	4.13	5.50	5.29	5.02	5.16
Tm	0.77	1.16	0.50	1.08	0.66	0.90	0.93	0.80	0.85
Yb	5.04	7.51	3.20	6.96	4.16	5.75	5.87	5.29	5.57
Lu	0.71	1.11	0.44	1.02	0.60	0.87	0.88	0.77	0.79
Hf	4.47	5.55	3.93	4.50	2.43	5.77	4.79	8.57	7.91
Ta	0.46	0.30	0.26	0.40	0.21	1.09	0.49	0.44	0.88
Pb	6.76	7.22	5.34	2.45	7.34	18.68	21.89	19.23	24.86
Th	4.03	2.75	2.07	0.93	0.75	15.75	18.31	14.52	15.42
U	1.04	1.34	0.68	0.31	0.22	4.01	4.54	3.40	3.77

* denotes total iron

and Fe₂O₃ with MgO. Al₂O₃ wt% generally behaves erratically showing no correlation with MgO wt%. Two trends are observed in the TiO₂, CaO and Fe₂O₃ v. MgO plots (Fig. 4), one at lower MgO wt% with a steep increase in the other major elements and the other which shows less variation in the other oxides with increasing MgO wt%. Sample REB166 is the most primitive basalt in the suite, with a MgO of 10.8 wt%, SiO₂ of 46.4 wt% and Fe₂O₃ of 1.0 wt%.

In Figure 5 selected trace elements are plotted against Zr. When immobile elements are plotted against Zr (itself immobile and incompatible in the basalts), a good correlation within the basalts indicates that the sequence of rocks are possibly co-genetic (Cann, 1970; Hastie *et al.* 2008). Many of the more immobile elements show a broad positive linear correlation with Zr (e.g. La), whereas Sc decreases as the lavas become more evolved (Fig. 5). These features suggest that the basalts may be derived from parent magmas that have been derived through similar melting conditions from a similar source.

The La/Yb ratios of the basalts range from 1.9 to 3.3. The basaltic samples generally have flat to slightly LREE-enriched chondrite-normalized REE patterns with a slight depletion in the HREEs (Fig. 6a). The basalts are somewhat enriched compared to N-MORB, particularly for the more incompatible elements on the left-hand side of the N-MORB-normalized plot and

generally have variable negative Nb anomalies, except sample REB166 (Fig. 6b). As the basalts become more evolved so they become more enriched in incompatible trace elements and develop a progressively more marked negative Eu anomaly (Figs 5e, 6b).

5.d. Dacite and rhyolite geochemistry

The evolved samples contain more Si and K along with less Ti, Ca and Fe than the basaltic rocks. The major element composition variations range from e.g. 64.7–76.1 wt% SiO₂ and from 1.3–6.3 wt% K₂O in a linear array (Fig. 4). The trace element variations v. Zr (Fig. 5) for the more evolved samples are more scattered than for the basalts, although a broad linear trend is observed for La and Nb (Fig. 5a, d). The Zr content increases from the basalts to the dacites before falling again in the rhyolites, which may indicate Zr saturation followed by fractionation. The lack of coherent trace element trends both between the basalts and the evolved rocks, and within the evolved rocks themselves is most likely a reflection of Zr's incompatibility in the basalts and dacites and compatibility in the rhyolites. This is especially evident from the Th–Zr variation diagram, which shows a co-genetic trend for the basalts, while the data for the rhyolites and dacites are more scattered (Fig. 5b).

The La/Yb ratio of the dacites varies from 3.8–7.3, while the rhyolites vary from 4.6–6.1. The rhyolites and

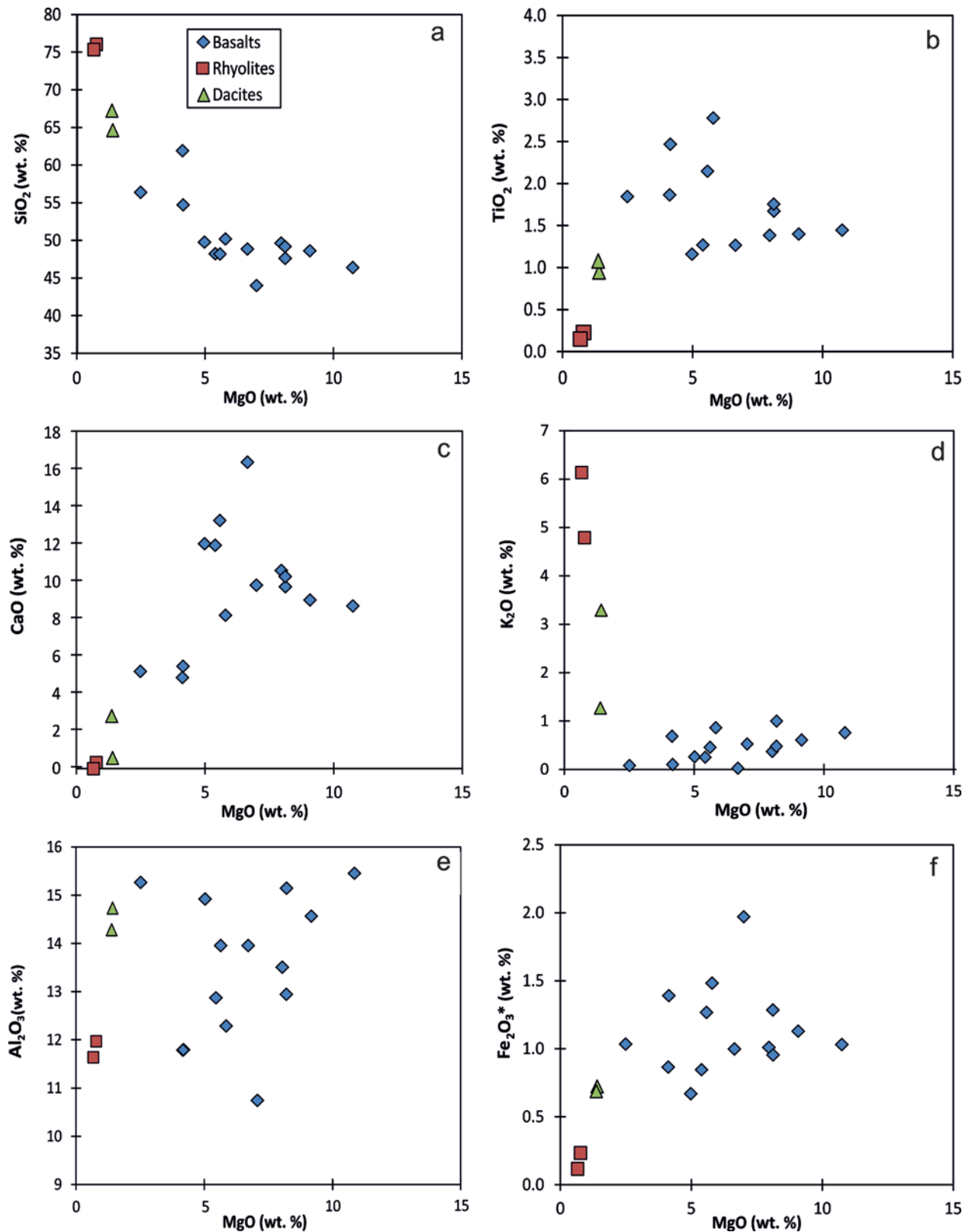


Figure 4. (Colour online) Bivariate plots of major element data against MgO (wt. %) for the Fishguard volcanic rocks.

dacites are significantly more enriched in the LREEs ($(\text{La}/\text{Sm})_{\text{CN}} > 3$) (chondrite normalized; Sun & McDonough, 1989) than the basalts ($(\text{La}/\text{Sm})_{\text{CN}} < 3$) but have similar, relatively flat, HREE patterns (Fig. 6a, b). All of the dacites and rhyolites possess negative

Nb anomalies (Fig. 6b). The more evolved rocks also show more marked negative Eu anomalies than the basalts indicating separation of plagioclase during low-pressure crystal fractionation from a more basic magma (Figs 5e, 6a).

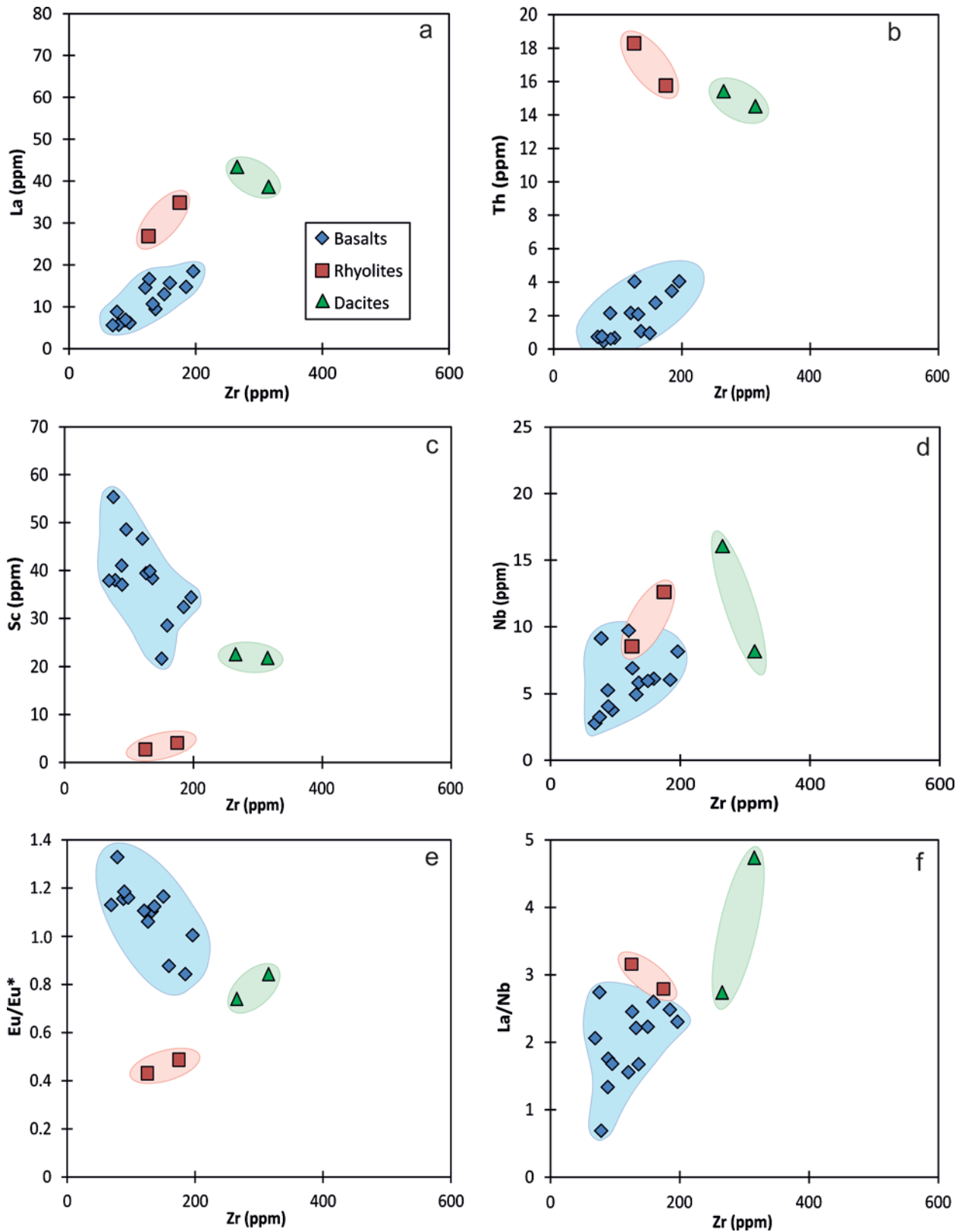


Figure 5. (Colour online) Bivariate plots of trace elements variation with Zr (ppm) for the Fishguard volcanic rocks.

6. Discussion

6.a. Mantle source composition

Modern-day back-arc basins are underlain by both oceanic and continental crust formed by either seafloor spreading, rifting of older arc or continental crust

(Sinton *et al.* 2003; Martinez *et al.* 2006). However, the relative proportions of these types of crust are often a matter of considerable debate (Stern, 2002). The formation of oceanic crust in back-arc basins is thought to be mainly controlled by two different melt generation processes: hydrous flux melting

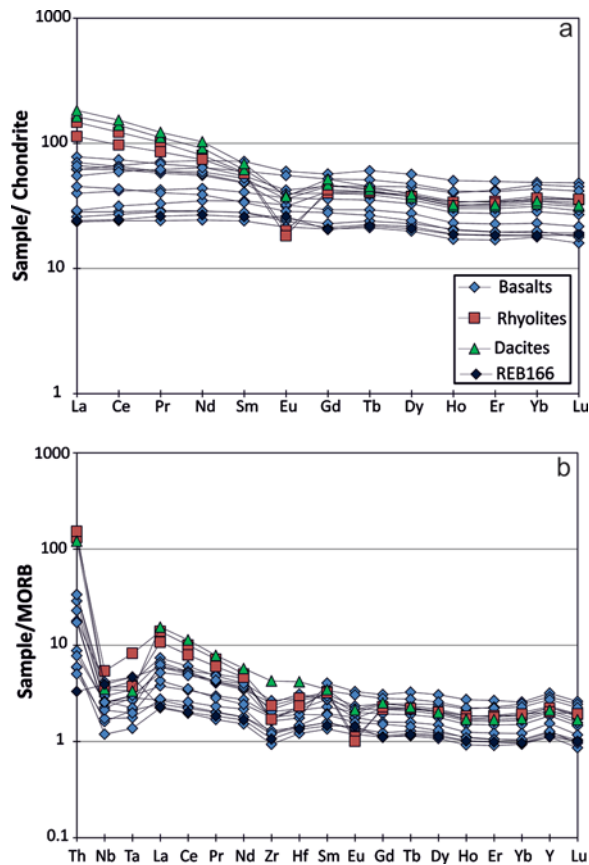


Figure 6. (Colour online) (a) Chondrite-normalized REE and (b) MORB-normalized trace element diagrams (normalizing values from Sun & McDonough, 1989). Sample REB166 is highlighted.

(e.g. Tatsumi & Eggins, 1995) and decompression melting during seafloor spreading (e.g. Langmuir, Klein & Plank, 1992). With increasing distance of the back-arc spreading centre from the subduction zone, decompression melting tends to dominate over subduction flux melting (e.g. Gribble *et al.* 1998; Sinton *et al.* 2003).

Factors contributing to the geochemical heterogeneity of back-arc basin basalts include variations in the underlying mantle in terms of its fertility, composition and degree of partial melting, lithospheric thickness and amount of water present in the system (Pearce & Stern, 2006). Variations in the subduction input, such as the nature and composition of the subducted materials, will also influence the geochemistry of lava erupted in the back-arc region. The melting, assimilation and crystallization history of the lavas will also contribute to the compositional diversity observed in back-arc basins. The influence of subduction zone fluids should be greatest during the early stages of basin opening and then diminish as the basin widens, although this is dependent on the geometry of the basin (Sinton *et al.* 2003; Martinez *et al.* 2006).

The magmas represented by the basalts of the Fishguard Volcanic Group were most likely derived from a shallow, relatively garnet-free, source (spinel lherzolite) as indicated by the flat HREE patterns. This is most likely reflective of the E–W extension of imma-

ture continental crust that occurred from the Tremadoc to Caradoc (485–448 Ma), resulting in locally subsiding grabens controlled by crustal discontinuities (Kokelaar, 1988).

More insights from the REE data for the rocks and so their source can be gained through the use of a Dy/Dy*–Dy/Yb plot (Fig. 7a). Dy/Dy* ($\text{Dy/Dy}^* = \text{Dy}_N/(\text{La}_N^{4/13} \cdot \text{Yb}_N^{9/13})$) is a measure of the concavity of a REE pattern (Davidson, Turner & Plank, 2013) and, in addition to helping determine source components, this diagram can help elucidate if amphibole has been significantly involved in the petrogenesis of a magma (either by fractionation or by being residual in the source). Figure 7a shows that the Fishguard lavas and intrusions plot mostly in the MORB field of the diagram and display a general trend of increasing Dy/Dy* with Dy/Yb. Only samples SB59 and SB54 trend towards the amphibole vector, indicating minimal involvement.

The Th/La–(Ce/Ce*)_{Nd} diagram (Fig. 7b) is used to determine the affinity of sedimentary slab components that have contaminated the source region of subduction zone rocks. The majority of the basalts plot in an array between N-MORB and the volcanic detritus field, with some of the more evolved basalts plotting within the continental detritus field, indicating a variable subduction component within the basalts. This suggests relative proximity to the continental subduction zone.

All except one of the samples analysed in this study (REB166) are displaced above the MORB–OIB array towards the continental arc region of the Th/Yb–Nb/Yb plot (Fig. 7c) further implying proximity to a subduction zone. The subducting slab does not retain Th and, therefore, an increase in its concentration in the mantle wedge, and so in back-arc basin magmas, is indicative of input from a subduction zone (Pearce, 2008). An increase in the Th/Yb ratio, therefore, implies an increasing subduction input, while an increase in the Nb/Yb ratio is more indicative of increasing depth of melting. It is clear that the Fishguard rocks show a variable subduction influence in the basalts with little change in melting depth, in agreement with Figure 7b. Figure 7b, c suggests that sample REB166 contains a minimal amount of subduction component. The sample, highlighted in Figure 6, also shows no Nb depletion or significant Th enrichment seen in the other samples. Typically back-arc basin basalts can contain variable amounts of subduction components (Pearce *et al.* 2005; Pearce & Stern, 2006). In the case of the Fishguard Volcanic Group the majority of the basalts contain a substantial subduction component. These components are derived during subduction by the release of fluids and/or sediments from the slab or may have been via inherited subduction components in the lithosphere, highlighting the complexity of the source.

6.b. Crustal processes

Bevins (1982) suggested that the various dacites, rhyolites and rhyolites exposed in the Porth Maen Melyn and Fishguard area were derived by crystal fraction-

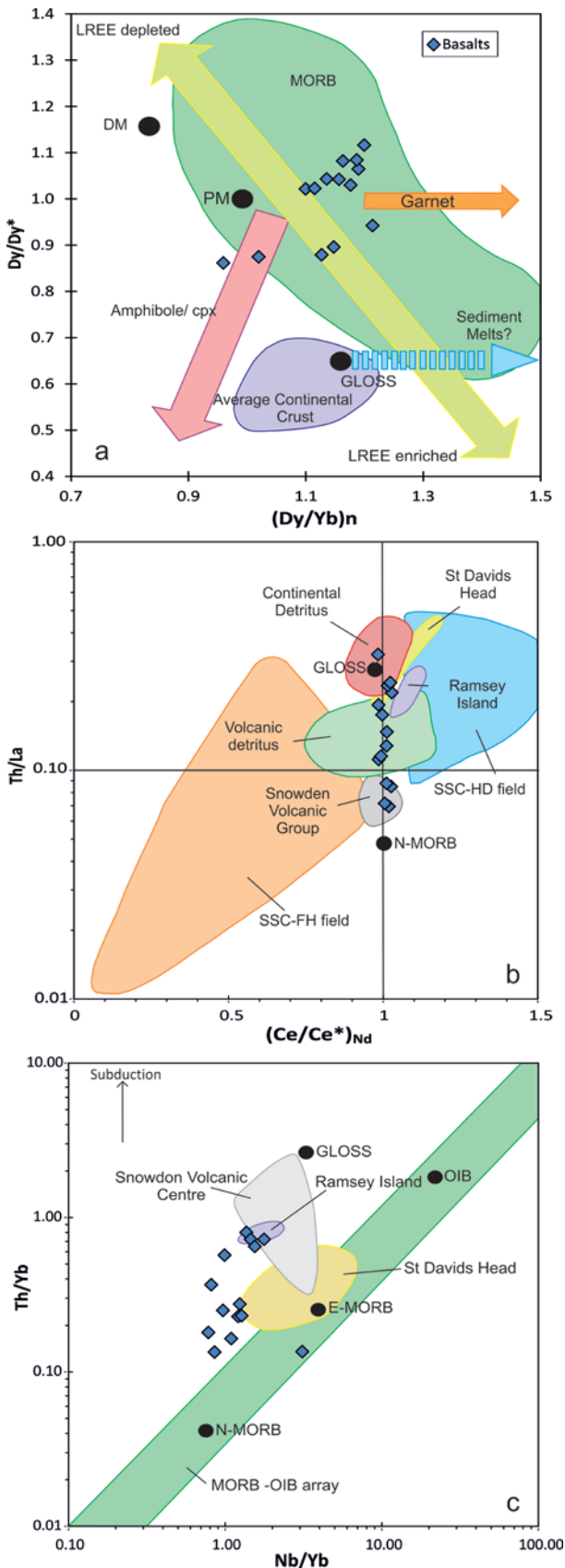


Figure 7. (Colour online) (a) A Dy/Dy^* – Dy/Y plot of Fishguard lavas adapted from Davidson, Turner & Plank (2013). DM – depleted mantle; PM – primitive mantle (Sun & McDonough, 1989); MORB – mid-ocean ridge basalt; GLOSS – average global subducting sediment (Plank & Langmuir, 1998). (b) Th/La – $(Ce/Ce^*)_{Nd}$ diagram (Hastie *et al.* 2013) showing the potential sedimentary slab components that may have

ation from the basic magmas. The relative roles of fractional crystallization from basalt and generation by crustal melting for the silicic rocks of the Ordovician marginal basins of Wales have been debated by many authors (Kokelaar *et al.* 1984b; Leat *et al.* 1986; Thorpe *et al.* 1993)

In order to test these different models both fractional crystallization and assimilation with fractional crystallization (AFC) modelling were carried out. Rayleigh fractional crystallization modelling was undertaken using sample LG3 as a possible parental magma as it has relatively high MgO (9.1 wt%) and also has low LREE contents. Those models were calculated using PELE, a PC platform version of the silicate liquid crystallization MELTS software program (Boudreau, 1999). The major element geochemical trends were modelled at different pressures and water content parameters, using a quartz–fayalite–magnetite (QFM) oxygen buffer to define oxygen fugacity (fO_2). The modelling at 1 kbar predicts initial crystallization of olivine and spinel, until ~12% crystallization at which point plagioclase begins to crystallize followed by clinopyroxene at ~39% crystallization. This sequence is generally consistent with that observed in the thin-sections. Most of the samples show ophitic clinopyroxene plagioclase relationships with some of the clinopyroxene also containing rounded pseudomorphs of what was previously olivine. The chemistry of this mineral assemblage predicted by PELE was then modelled at 10% fractionation intervals using the relevant distribution coefficients (Rollinson, 1993).

The results presented in Figure 8 are of the models that best predict the major geochemical trends observed in the data, i.e. low-pressure fractional crystallization (1 kbar) in a magma that was either anhydrous or contained 1% H_2O . The basalt trend is more accurately modelled than the dacite/rhyolite data. The models can generally predict the SiO_2 and K_2O trends of the basalts and some of the more evolved rocks but cannot replicate the highest values. The models predict the low CaO trend of the basalts but have higher CaO than the dacites and rhyolites. The high CaO trend is most likely a result of alteration (Bevins, 1982). The FeO trend, however, is poorly replicated by the models. A low-pressure magma chamber model is in accordance with previous studies (Bevins, Lees & Roach, 1991) but neither fractional crystallization model conclusively fits the observed data.

contaminated the source region. SSC-HD – slow sediment clay – hydrogenous; SSC-FH – slow sediment clay – fish debris/hydrothermal. (c) The Th/Yb – Nb/Yb diagram from Pearce (2008). An enrichment in Th relative to the equally incompatible Nb acts as an effective proxy of subduction input. Representative fields for other Welsh lower Ordovician volcanic complexes are also plotted on (b) and (c) for comparison. The data for Ramsey Island and St Davids Head were obtained from Bevins *et al.* (1991) and the Snowdon data from Thorpe *et al.* (1993). N-MORB – normal mid-ocean ridge basalt; E-MORB – enriched mid-ocean ridge basalt; OIB – ocean island basalt.

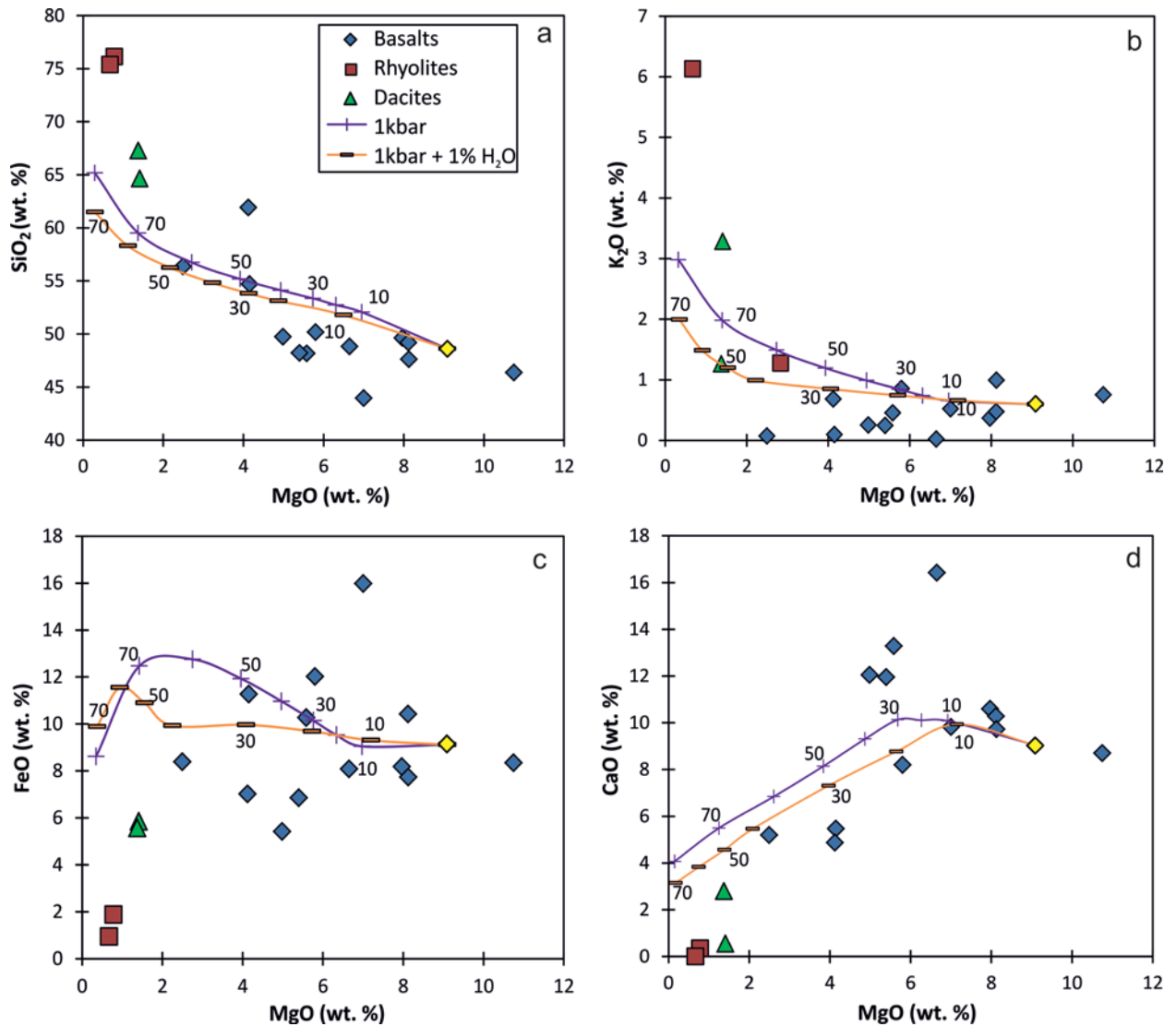


Figure 8. (Colour online) Bivariate diagrams of selected major elements v. MgO for the Fishguard volcanic rocks along with modelled fractional crystallization trends (1 kbar anhydrous and 1 kbar with 1 % H₂O added) for a parental magma with a composition of sample LG3. Markers on the modelled trends are at intervals of 10% crystallization.

AFC modelling (DePaolo, 1981) was carried out for trace elements at 1 kbar (Fig. 9). A significant limitation to the model is that Zr is incompatible in all instances, whereas in reality it is compatible in the more evolved rocks, meaning that their compositions are not reproduced in the models. Another limitation to the AFC models is that the exact nature of any potential contaminant is not known. An average composition for felsic continental crust has been used (from Rudnick & Gao, 2003), which represents a potential fusible crustal contaminant.

Marked enrichments in incompatible elements (particularly Yb, Tb, Y) observed in rhyolites and dacites (Fig. 9a, c, d) can be replicated by AFC modelling, especially with higher crustal assimilation. The models cannot, however, replicate the elevated Th, Yb, Tb and Y concentrations of the basalts nor does any one single curve match the trend shown by the rest of the samples (Fig. 9b). These models do, however, suggest a shift

from initial fractional crystallization in the most primitive basalts to assimilation fractional crystallization in the more evolved basalts.

6.c. Tectonic reconstruction

The evidence discussed in the previous section suggests that the rocks in this study (a) have been subjected to the influence of subduction zone components; (b) have undergone some crustal contamination; and (c) the basalts have a source that is compositionally similar to MORB, as evidenced by Figure 7a.

The mantle source composition for the primitive magmas of the Fishguard Volcanic Group has been determined to be a mixture of MORB-like source mantle and subducted sediment. Flat HREE patterns indicate melting took place in the spinel stability field at shallow depths (<60 km) and so, along with the above,

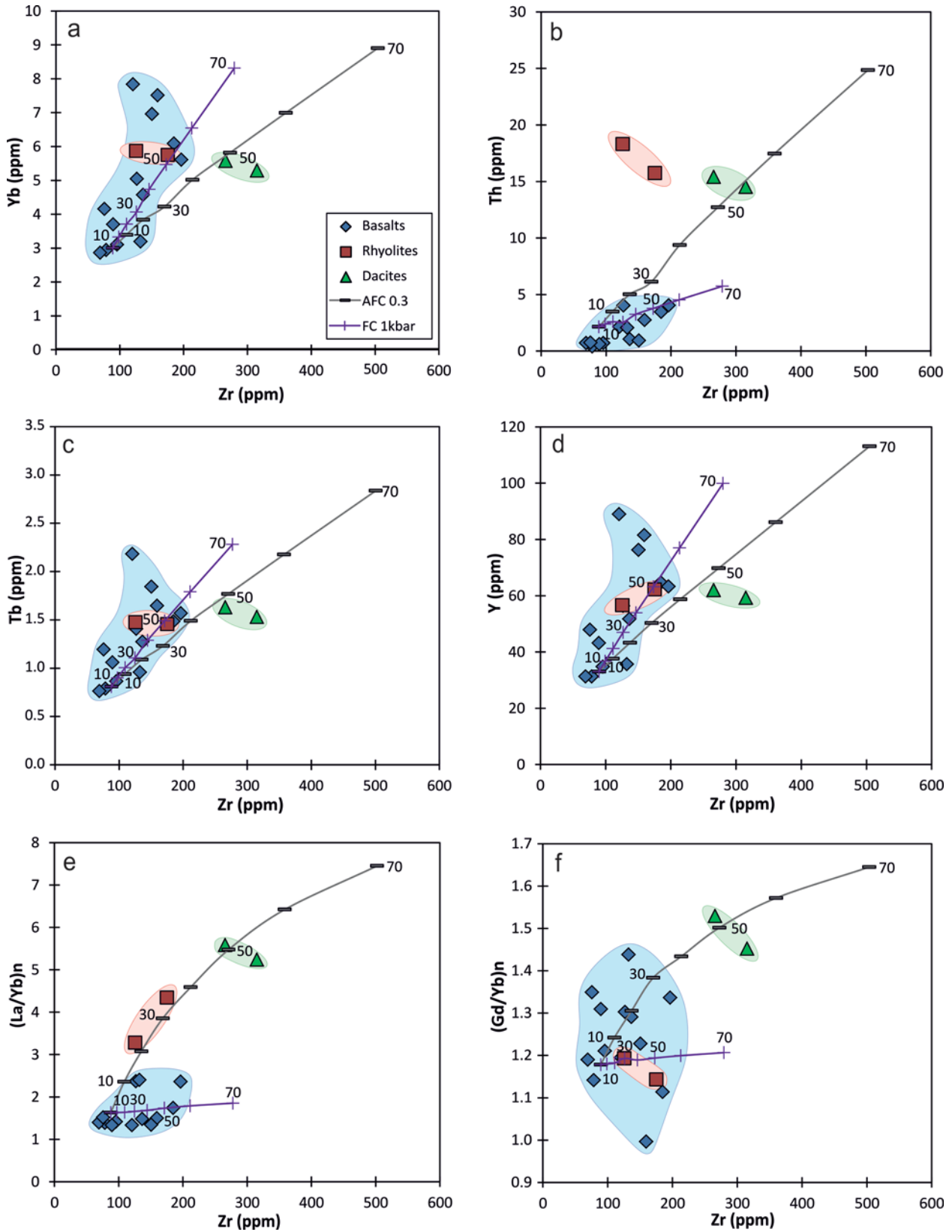


Figure 9. (Colour online) Bivariate diagrams for representative trace elements and incompatible trace element ratios showing the results for AFC and fractional crystallization, where 0.3 AFC is equal to 30% additional contamination and represents the model that best replicates the geochemical trend of the Fishguard Volcanic Group.

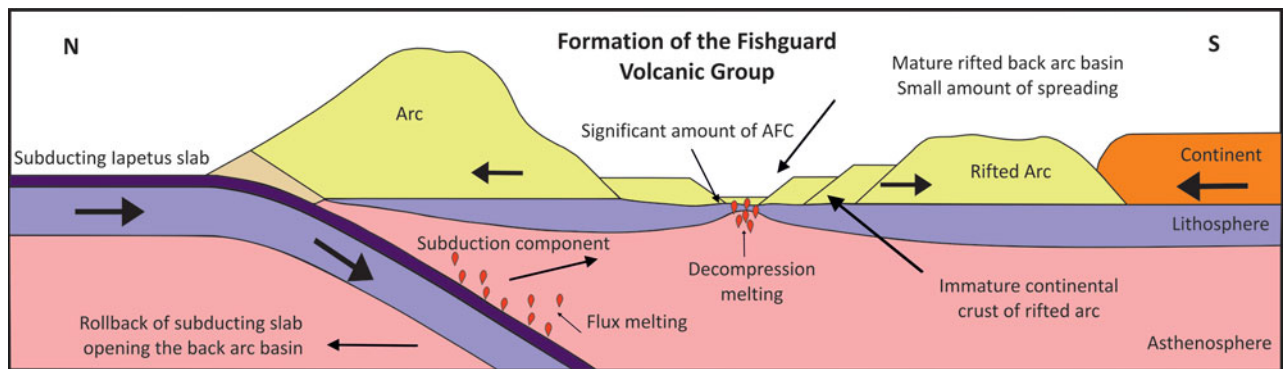


Figure 10. (Colour online) Proposed model for the formation of the Fishguard Volcanic Group. The diagram shows the tectonic configuration of the Iapetus slab subducting below the Avalonia continent, with rollback of the subducting slab facilitating the rifting of the arc and opening of the back-arc basin. This rifting leads to decompression melting in the structurally weaker parts of the basin; these magmas mix with melts associated with fluids from the subducting sediments. A small amount of crustal contamination occurs as the melts rise through the rifted arc crust.

indicate contamination of a spinel lherzolite source with subduction components. Contamination of the source by continental volcanic detritus (Fig. 7b) signifies an arc-proximal setting close to a continental margin (e.g. Sinton *et al.* 2003; Martinez *et al.* 2006). In addition to this, the presence of spatially and temporally close acidic and intermediate rocks and the lack of formation of true oceanic crust (Kokelaar *et al.* 1984b) indicate proximity to a volcanic arc. The immature continental crust on which the Fishguard basin formed (Kokelaar *et al.* 1984b) may have been part of a rifted arc system, which originated from earlier arc volcanism in Tremadoc time represented by the Trefgarn Volcanic Group (Kokelaar *et al.* 1984a).

The suite of investigated rocks shows a compositional range through basalts, basaltic andesites, dacites and rhyolites. The rocks in this suite of lavas and intrusions are most likely compositionally similar magmas, with any scatter likely owing to variable subduction inputs, fractional crystallization and AFC. Fractional crystallization at 1 kbar can explain many of the trends observed in the data. Low-pressure fractional crystallization also generally agrees with the estimated source depth and with previous studies such as Bevins, Lees & Roach (1991). There may have also been a hydrous component in the form of fluids or hydrous minerals (Fig. 8) present during fractional crystallization, which is consistent with a subduction zone setting (Stern, 2002). AFC modelling indicates that crustal contamination also played a significant role in the formation of the more evolved rocks. Furthermore, crustal contamination reinforces the interpretation that the basin was formed on rifted volcanic arc crust (Kokelaar *et al.* 1984b; Martinez *et al.* 2006).

The Fishguard Volcanic Group is, therefore, likely to have formed in a back-arc basin setting in which a compositionally continuous and genetically linked suite of lavas were erupted. It is suggested that the Fishguard Volcanic Group formed in a back-arc basin where ex-

tensive rifting but no true spreading (and oceanic crust generation) had yet occurred.

6.c.1. Regional implications

Other Ordovician lavas erupted in the Welsh marginal basin show geochemical similarities to the Fishguard Volcanic Group. The Ramsey Island rhyolites (Middle Arenig) (Kokelaar *et al.* 1984b) in particular are markedly compositionally similar to the Fishguard Volcanic Group (e.g. Fig. 7b, c), which may be a reflection of their spatial and temporal proximity (Bevins, Lees & Roach, 1991). The rocks of the Snowdon Volcanic Group, North Wales (Fig. 1) (Arenig – early Caradog) (Kokelaar *et al.* 1984b) are enriched in incompatible elements (Fig. 7c) with moderate to marked Fe enrichments and are transitional between tholeiitic and calc-alkaline in composition (Kokelaar *et al.* 1984b). Figure 7c shows that the rocks from the Snowdon Volcanic Group also contain generally higher Th/Yb ratios highlighting the more pronounced influence of subduction owing to their closer proximity to the volcanic arc (e.g. Sinton *et al.* 2003). This may be a reflection of the control of crustal discontinuities (steep fractures at shallow levels of considerable length that have undergone repeated tectonic activity) on the volcanic location and development (Kokelaar, 1988). The Fishguard Volcanic Group by comparison shows marked Fe enrichment (Kokelaar *et al.* 1984b) and a tholeiitic to tholeiitic–calc-alkaline transitional trend.

Figure 10 illustrates the proposed tectonic model for the origin and evolution of the Fishguard Volcanic Group. The proposed model is that the Fishguard Volcanic Group formed in a back-arc basin in which rifting and extension of immature continental crust (which may represent rifted arc crust) had occurred. The locus of extension most likely occurred between the active and rifted arc, where the system is rheologically weakest (Sdrolias & Müller, 2006). The magmas originated

partially from flux melting in the mantle wedge, with this melting facilitated by fluids expelled from subducting slab sediments. Decompression melting at relatively shallow depths, associated with the rifting of the basin also took place. The magmas underwent fractional crystallization, during which crustal contamination from the immature continental crust of the rifted arc took place.

There are several other known Ordovician Avalonian terranes that have comparable magmatism and originated in similar tectonic settings to the Welsh marginal basin rocks. Similar terranes from the southern flank of the Iapetus include the Antigonish Highlands Avalonian terrane in Nova Scotia, Canada, and the Avoca volcanic rocks, Ireland; both formed owing to rifting within an overall arc environment (McConnell, Stillman & Hertogen, 1991; Murphy, Hamilton & LeBlanc, 2011). These comparable origins, therefore, reinforce the suggested model of formation for the Fishguard Volcanic Group.

7. Conclusions

(1) The Fishguard Volcanic Group formed in a back-arc basin in close proximity to a subduction zone.

(2) Geochemical evidence and modelling indicates a shallow (garnet-free) lherzolite source for the Fishguard Volcanic Group. Subduction inputs and low-pressure (1 kbar) fractional crystallization are the more influential processes in the petrogenesis of the basalts, while crustal contamination was a significant process in the formation of the more evolved rocks of the Fishguard Volcanic Group.

(3) The immature continental crust nature of the basin may be derived from a rifted arc crust (Kokelaar *et al.* 1984b), which, coupled with the suggested shallow source region, indicates that previous extension had occurred in the basin. This is consistent with the evidence for earlier volcanic arc activity in this region during Tremadoc time (485–478 Ma) (Kokelaar *et al.* 1984b).

(4) It is, therefore, suggested that the Fishguard Volcanic Group was generated in a back-arc basin setting where extensive rifting (but no seafloor spreading) has occurred (Fig. 10).

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Supplementary material

To view supplementary material for this article, please visit <http://dx.doi.org/10.1017/S0016756815000461>.

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