Analytical Methods

Whole Rock: Analysis of Trace Elements and $^{87}Sr/^{86}Sr$ of Rock Powders

Analysis of whole rock powders was undertaken at the Arthur Holmes Isotope Geology Laboratory (AHIGL) which forms part of NCIET (Northern Centre for Isotopic and Elemental Tracing) at Durham University, UK and at UCLA, California. Samples collected in the field were made as fresh and unaltered as possible by chipping off weathered surfaces using a rock hammer. The sample was crushed in a fly-press to grains <2 cm3. Any remaining, visibly altered material was removed at this point. The crushed sample was then powdered in an agate ball mill.

For Sr elemental analysis, 0.1 g of sample powder was dissolved using digestion techniques involving HF and HNO_3 SpA acid. The sample solution was run for trace elements on an inductively coupled plasma mass spectrometer (ICPMS, the Perkin Elmer-Sciex Elan 6000 instrument at Durham University). During the period of study, 6 analyses of the international standard W2 was carried out, for Sr: 200.93 ppm ± 1.62 (2σ). This is in excellent agreement with the accepted value; 196 ppm ± 10 (2σ).

For Sr-isotopic analysis, 0.1 g of sample powder was dissolved using standard digestion techniques involving HF and HNO_3 SpA acid. Sr was separated from the sample solution using Sr-spec resin columns (see Charlier et al., 2006). Sample solutions were run for their $^{87}Sr/^{86}Sr$ composition by plasma ionisation multicollector mass spectrometry (PIMMS) using the Thermo Scientific Neptune instrument at Durham University and by thermal ionisation mass spectrometry (TIMS) using the VG Sector 54-30 mass spectrometer at UCLA. During the period of study at Durham University, 7 analyses of the international Sr standard NBS987 were carried out. The average $^{87}Sr/^{86}Sr$ was 0.710254 ± 0.000013 (2σ). 15 standards were run at UCLA and measured at 0.710220 ± 0.000013 (2σ).

Electron Probe: Analysis of Major Elements in Glass

Electron microprobe analyses were performed at the School of Geosciences, University of Edinburgh using the CAMECA SX100 microprobe. Samples were analysed with a 10 nA electron beam accelerated to 15 kV with a spot size of 5 µm. The CAMECA SX100 software automatically performed background corrections and standard "PAP" corrections (e.g. Pouchou and Pichoir, 1988). Sodium (Na) was analysed first so that loss through volatilisation was minimised.

Microdrilling: Analysis of Trace Elements and $^{87}Sr/^{86}Sr$ in Glass

In-situ sampling of quenched anatectic glass was undertaken at the AHIGL at Durham University, UK. A detailed account of the following technique is presented by Charlier et al., 2006. The New Wave Micromill was used throughout this study and consists of an integrated binocular microscope, stage and drill which can all be operated from a computer. Samples were prepared on 100-µm-thick sections and photomicrographs were used to select suitable sampling sites with care taken to avoid fractures, bubbles and crystals. Samples were drilled as an array of points (14-25 points of 40 µm depth). Each point was drilled twice. Microsampling was undertaken in a drop of ultra pure MilliQ water into which the drilled sample was collected. The suspended sample was then pipetted onto a gold boat and dried down. Blanks were prepared by drilling to 0 µm depth within a water drop and subsequently treated identical to the samples.

The dried-down sample powder was then dissolved using ultra pure acids (see Charlier et al., 2006). An aliquot of 20 µl of sample solution (from a total of 200 µl) was added to 480 µl of 3M ultra pure HNO_3. This 500 µl solution was run for trace elements on an inductively coupled plasma mass spectrometer (ICPMS, the Thermo Scientific Element II instrument) at Durham University. The remaining 180 µl of sample solution was run through micro-Sr column chemistry. For detailed analytical procedure see Font et al., 2008. Blanks contained less than 26 pg for all analysed elements with strontium blanks less than 2 pg (n=3). During the period of study 3 analyses of the international standard W2 was carried out. Average measured Sr concentrations (for 1000 times dilution as was appropriate to the sample size) was 0.42 ppb ± 0.04 (2σ) which is in agreement with the accepted value of 0.39 ppb. Samples were run for their $^{87}Sr/^{86}Sr$ composition by thermal ionisation mass spectrometry (TIMS) using the Thermo Scientific Triton instrument at Durham University. Analytical procedures and information regarding data correction is presented by Font et al., 2008. During the period of study, 19 analyses of the international Sr standard NBS987, on a range of load sizes (600 to 1 ng), were carried out. The average $^{87}Sr/^{86}Sr$ was 0.710246 ± 0.000015 (2σ). This is in excellent agreement with the value reported by Thirlwall (1991) of 0.710248 ± 0.000023 (2σ, n=427).

References

Charlier, B. L. A., Ginibre, C., Morgan, D., Nowell, G. M.,Pearson, D. G., Davidson, J. P. and Ottley, C. J., 2006, Methods for microsampling and high-precision analysis of strontium and rubidium isotopes at single crystal scale for petrological and geochronological applications: Chemical Geology, v. 232, p. 114-133.

Font, L., Davidson, J. P., Pearson, D. G., Nowell, G. M., Jerram, D. A. and Ottley, C. J., 2008, Sr and Pb isotope micro-analysis of plagioclase crystals from Skye lavas: an insight into open-system processes in a flood basalt province: Journal of Petrology, v. 49, p. 1449-1471.

Pouchou, J-L., and Pichoir, F., 1988, A simplified version of the "PAP" model for matrix corrections in epma, in DE Newbury, ed. Microbeam Analysis, p. 315-318.

Thirlwall, M.F., 1991, Long-term reproducibility of multicollector Sr and Nd isotope ratio analysis: Chemical Geology (Isotope Geoscience Section) v. 94, p. 85-104.

Xenolith Petrography for Samples Run for Geochemical Analyses

QNX03, QSX04: Microgranite

Sampled microgranites are coarse grained (0.2-4.5 mm) and consist of biotite (5-10%), plagioclase (15-25%), quartz (40-50%), orthoclase (15-20%) and minor opaque phases (<5%). Micrographic intergrowth textures are observed between quartz and plagioclase and quartz and orthoclase crystals. Quartz occurs as small (<0.4 mm) sub rounded to rounded inclusions in both plagioclase and orthoclase feldspar and displays consertal textures where grain boundaries of larger crystals (up to 3.2 mm) have intergrown.

PAX07, PAX11: Diorite

Sampled diorites are coarse grained (0.4-2 mm) consisting of hornblende (10-15%), biotite (30-40%), quartz (10-15%) plagioclase (30-35%), minor orthoclase (<7%), minor opaque phases (ilmenite and magnetite, <10%) and rare (non-ubiquitous) felsic glass (<2%). Occasionally, quartz overgrowths are visible on sub-rounded orthoclase cores. These rocks exhibit an inequigranular, granoblastic texture with biotite porphyroblasts often displaying alteration to orthopyroxene, which forms fine grained (<0.3 mm) aggregates, at crystal boundaries. This is consistent with the breakdown of biotite to orthopyroxene (plus melt).

PAX01, PAX12: Garnet-Sillimanite Gneiss

Both are coarse grained (up to 3.9 mm) and are characterised by the high modal abundance of quartz (55-65%), garnet (10-15%) sillimanite (10-15%) in the form of fibrolite, biotite (10%) and plagioclase (5-10%). Accessory phases include anatase, monazite and zircon. Quenched glass (<3%) is also present (rarer in PAX01).

QNX02, PAX03, PAX14: Garnet-Sillimanite Granulite

In these samples quartz (50-60%), plagioclase (up to 10%), garnet (10-15%), fibrolite (15-20%, fibrous form of sillimanite), rare biotite (<10%), minor opaque phases (<5%) and minor rutile, which occurs as rare needles in garnet (<2%) are present with accessory monazite and zircon. Quartz grains are often intergrown displaying consertal textures at their boundaries. A few samples exhibit evidence for partial melting in the form of quenched glass in which very fine grained (<200 µm) acicular crystals of anatase (TiO_2) are present.

Rarer Sampled Lithologies

Garnet Mica Schist

Sampled garnet-mica-schists comprise of biotite (up to 15%), fibrolite (20-30%), garnet (15-20%), plagioclase (5-10%), quartz (35-45%) and accessory zircon. These samples are characterised by regular alternating layers of a few millimetres in thickness indicative of ductile deformation: dark biotite-sillimanite ± garnet porphyroblasts melanosomes and quartzofeldspathic leucosomes.

Garnet Granulite

Samples consist of quartz (40-50%), plagioclase (10-15%), garnet (15-20%), rare cordierite (<5%), rare biotite (<5%), altered kyanite (10-15%), minor opaque phases (<2%) and accessory monazite and zircon. Quartz occurs in bands (1.5 mm in width) where it is notably coarser grained (up to 1.1 mm) and as inclusions in garnet porphyroblasts.

Gneiss

Samples contain quartz (35-45%), biotite (15-25%), plagioclase (20-25%), alkali feldspar (5-10%), rare muscovite (<5%) minor opaque phases (<2%) and accessory zircon. Biotite is intermittently present in bands (up to 1 mm in width) between quartzofeldspathic dominated portions of the rock which produce the classic "gneissic" texture.

Table DR1. Range of EC-AFC model parameters used in Figure 1C

1. Thermal parameters	
Magma liquidus temperature Tlm	1100 – 1200°C
Magma initial temperature Tm0	1100 – 1200°C
Assimilant liquidus temperature Tla	1100 – 1200°C
Assimilant initial temperature Ta0	600 – 700°C
Assimilant solidus temperature Ts	700 – 800°C
Equilibration temperature Teq	710 – 877°C
Crystallization enthalpy Δhcry	350000 – 3960000 J/kg
Isobaric specific heat of magma Cpm	1452 – 1484 J/Kg per K
Fusion enthalpy Δhfus	354000 – 370000 J/kg
Isobaric specific heat of assimilant Cpa	1388 – 1400°C
2. Compositional parameters	
Magma initial concentration (Sr, ppm) Cm0	945
Magma isotopic ratio (87Sr/86Sr) εm	0.7041
Magma trace element distribution coefficient Dm	1 –1.5
Assimilant initial concentration (Sr, ppm) Ca0	131.3; 194.7; 343
Assimilant isotopic ratio (87Sr/86Sr) εa	0.722624; 0.732878; 0.7363760
Assimilant trace element distribution coefficient Da	0.2 – 1

Note: Only ranges for the curves plotted in Fig. 1C are documented here. Additional solutions are possible by implementing a broader range of magma and assimilant parameters, use of a more primitive mantle-melt (e.g., ID1 of Nye and Reid, 1986) which is inferred to represent a primitive arc-mantle melt) or more primitive compositions found across the Andean Cordillera as well as further varying the compositions of the crustal assimilant.

Reference

Nye, C.J. and Reid, M.R., 1986, Geochemistry and least fractionated lavas from Okmok Volcano, central Aleutians: implications for arc magma genesis: Journal of Geophysical Research, v. 91, p. 10271- 10287.

Quillacas lavas (whole rock)

	$^{87}Sr/^{86}Sr$	Sr (ppm)	SiO_2 (wt. %)
QNL01	0.710122	450.6	60.34
QNL02	0.709885	464.9	59.98
QSL01	0.709128	478.2	58.17
QSL02	0.709255	479.4	58.31
QSL03	0.710002	443.2	59.86
QSL04	0.709751	459.0	58.72
QSL05	0.709871	445.9	59.99
QSL06	0.710182	452.7	60.04
QSL07	0.709292	482.0	58.83
QSL08	0.709694	471.4	59.12
QSL09	0.709372	475.8	58.57

Pampas Aullagas lavas (whole rock)

	$^{87}Sr/^{86}Sr$	Sr (ppm)	SiO_2 (wt. %)
PAL01	0.716691	350.1	64.78
PAL02	0.716947	344.9	63.14
PAL03	0.714015	440.6	62.68
PAL04	0.712261	525.9	59.40
PAL05	0.713657	582.0	61.83

Xenolith (whole rock)

	$^{87}Sr/^{86}Sr$	Sr (ppm)
PAX 01	0.719380	33.1
PAX 03	0.722624	343.0
PAX 07	0.712595	388.4
PAX 11	0.710481	416.4
PAX 12	0.717314	18.5
PAX 14	0.732878	194.7
QNX 02	0.736760	131.3
QNX 03	0.712017	301.7
QSX 04	0.712014	307.1

Major element composition of sampled glass. Values reported in wt. %

	SiO_2	K_2O	Na_2O	Al_2O_3
1	73.24	4.90	0.99	14.30
2	74.13	4.83	1.04	13.81
3	74.43	4.77	1.05	14.52
4	75.44	5.06	1.08	14.17
5	74.25	4.51	1.03	14.32
6	74.04	4.66	1.02	13.74
7	74.21	4.49	1.10	14.14
8	72.98	4.73	1.11	14.28
9	72.27	4.20	0.85	14.32
10	73.72	4.68	1.11	14.43
11	73.29	5.03	1.09	14.28
12	73.07	4.72	0.89	14.35
13	72.48	4.85	0.86	14.38
14	73.40	4.73	0.86	14.25
15	73.18	5.12	1.04	14.46
16	73.14	4.86	0.96	14.25
17	72.97	5.12	1.10	14.23
18	73.78	4.94	1.03	13.85
19	72.78	5.04	0.99	13.76
20	72.30	5.32	0.97	13.81
21	73.28	5.01	0.91	13.78
22	73.41	4.94	1.05	14.29
23	73.44	4.87	0.93	13.78
24	71.82	5.43	0.92	14.22
25	72.61	5.09	0.96	13.83
26	71.30	4.80	0.82	14.20
27	72.79	5.06	0.95	13.92
28	72.87	4.57	0.95	14.27

Trace element and Sr-isotopic compositions of BC93PAX12 and sampled glass. $^{87}Sr/^{86}Sr_i$ corrected for Pliocene ages of lava eruption. (values reported in ppm unless stated otherwise)

	Whole rock	Glass					
	BC93PAX12	1	2	3	4	5	6
Ba	138.4	357.1	563.6	520.5	1893	699.2	146.5
Rb	27.3	101.8	172.2	178.4	226.6	236.1	84.3
Th	7.3	2.2	2.2	2.5	4.7	3.8	4.6
U	1.4	0.8	1.4	1.3	2	1.6	2.2
Nb	17.1	4	1.5	1.5	4	2.6	4.6
La	22.4	9	10.8	10.7	21	15	14.9
Ce	46	20.7	30.4	29.9	49.6	37.4	66.8
Sr	18.5	34.7	56.3	32.3	107.2	37.1	37.2
Nd	22.8	12.2	15.4	16.3	26.9	21.4	18
Sm	4.7	2.9	3.9	4	6.2	5.3	3.5
Zr	32.8	54.9	112.1	103.8	135.2	119.1	89.7
Hf	1.1	1.2	2.9	2.6	3.2	2.9	2.2
Ti (wt. %)	0.3	0.3	0.3	0.3	0.5	0.4	0.3
Tb	0.8	0.4	-	0.5	0.9	-	0.5
Y	30.2	7.6	9.8	11	19.6	16.7	21
Yb	5.7	0.3	0.4	0.5	0.7	0.7	1.8
$^{87}Sr/^{86}Sr$	0.717314	0.717582	0.720943	0.725214	0.724592	0.728091	0.716588
$^{87}Sr/^{86}Sr_i$	-	0.717354	0.720705	0.724784	0.724427	0.727596	0.716412

29	71.97	4.90	0.84	13.45
30	73.37	5.63	1.04	14.23
31	69.81	4.76	0.95	20.70
32	73.12	5.35	0.99	14.08
33	72.07	5.24	1.01	13.49
34	73.49	4.91	0.99	14.14
35	73.43	5.08	0.90	14.10
36	72.23	4.04	0.48	14.00
37	74.28	4.30	0.83	13.83
38	74.25	5.12	1.02	13.79
39	73.63	5.23	0.98	14.13
40	72.26	4.70	0.99	14.49
41	73.70	5.17	0.95	14.31
42	73.94	5.03	0.95	14.12
43	72.41	4.71	0.91	13.77
44	74.20	5.41	1.08	13.93
45	72.69	4.68	0.87	14.24
46	74.01	4.79	0.84	13.52
47	72.22	4.70	0.84	13.99
48	72.50	4.58	0.82	13.98
49	72.97	4.94	0.93	13.54
50	74.37	5.09	1.09	13.82
51	74.41	4.70	0.89	14.00
52	72.61	4.87	0.94	14.09
53	73.46	4.96	1.18	13.10
54	73.32	4.67	1.03	14.02
55	73.22	4.79	1.08	14.13
56	72.61	5.11	1.10	14.29
57	74.14	4.84	1.00	14.19
58	73.46	5.09	1.03	14.32
59	72.44	5.21	1.02	13.58
60	72.12	4.68	1.09	13.85
61	74.22	5.03	1.17	14.11
62	74.04	4.76	0.93	14.19
63	73.46	5.17	1.13	13.72
64	73.51	5.09	1.12	14.04
65	73.46	4.93	1.14	14.13
66	73.12	4.76	1.05	14.47
67	73.64	5.08	1.28	14.05
68	72.18	4.91	1.18	14.10
69	72.39	5.05	1.16	13.48
70	72.96	4.66	1.08	13.74
71	74.25	5.03	1.20	14.27
72	72.61	4.87	0.97	13.95
73	73.94	4.73	0.85	14.42
74	72.39	4.53	1.00	14.08
75	72.79	4.61	0.93	13.69
76	73.72	4.91	0.94	14.03
77	72.02	4.62	0.95	13.86
78	73.05	4.90	1.02	13.87
79	73.79	4.62	0.93	13.90
80	73.67	5.03	1.07	13.95
81	73.15	5.05	1.13	13.75

82	72.80	4.70	1.10	13.76
83	72.51	4.23	0.86	13.97
84	75.39	3.80	0.75	13.97
85	73.83	4.71	0.90	14.47
86	75.03	4.60	0.89	14.00
87	74.37	4.99	1.01	14.28
88	72.65	5.34	1.04	13.76
89	74.24	4.10	0.83	13.76
90	73.42	4.62	0.88	14.31
91	72.60	4.94	1.01	13.45
92	72.34	5.09	1.11	14.29
93	73.57	5.19	1.07	14.03
94	73.65	4.72	0.91	14.50
95	72.85	5.11	1.13	13.79
96	72.51	5.21	1.10	13.87
97	74.46	1.55	0.37	14.25
98	71.99	4.99	0.84	13.98
99	73.50	4.85	0.82	14.20
100	71.44	5.00	0.89	13.57
101	72.61	4.77	0.97	13.60
102	73.41	4.89	0.96	14.90
103	72.96	5.05	0.99	14.61
104	73.49	4.54	0.96	14.08
105	72.99	4.94	1.06	13.80
106	73.02	4.99	1.05	14.11
107	72.91	5.16	1.18	14.21
108	73.15	5.22	1.22	14.15
109	72.59	4.51	0.93	14.00
110	73.06	5.00	1.16	14.14
111	73.88	4.62	0.95	14.12
112	72.39	4.69	0.92	13.85
113	73.12	4.53	0.92	14.13
114	73.36	4.91	1.11	13.77
115	73.10	4.18	0.96	14.43
116	73.23	5.26	1.21	14.19
117	71.46	4.85	0.98	13.39
118	71.19	4.34	0.97	13.88
119	71.92	4.70	1.08	13.50
120	74.26	5.05	1.07	14.29
121	73.01	4.70	1.09	14.31
122	74.03	5.08	1.11	14.53
123	72.78	4.66	0.97	14.50
124	72.51	4.74	0.96	14.37
125	74.35	4.51	0.95	15.18
126	74.83	4.93	1.11	14.02
127	74.19	4.74	1.15	13.94
128	73.50	4.57	1.07	13.56
average	73.19	4.83	0.99	14.10
1σ	0.875045411	0.412187305	0.12597547	0.665944
2σ	1.750090823	0.82437461	0.25195094	1.331887