Earth and Planetary Science Letters, 24 (1974) 105–112
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A COMPARISON OF ZIRCON U–Pb AND WHOLE-ROCK Rb-Sr SYSTEMS IN THREE PHASES OF THE CARN CHUINNEAG GRANITE, NORTHERN SCOTLAND

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Received July 8, 1974

Revised version received September 20, 1974

Zircons from two biotite granite units, the Inchbae rock and Lochan a' Chairn rock, from the 560-m.y. old Carn Chuinneag granite contain excess radiogenic lead. No excess radiogenic lead has been found in a third granite unit – the riebeckite gneiss. The excess radiogenic lead is attributed to zircon xenocrysts which have partially survived the formation of the granite magma and been incorporated in newly crystallizing zircon. The zircon U–Pb systems from the Inchbae rock suggest 1500 ± 200 m.y. as the age of its source rocks. The absence of excess radiogenic lead in the riebeckite gneiss zircons is attributed to either the progressive exclusion of zircon xenocrysts during formation of the Lochan a' Chairn rock and riebeckite gneiss magmas or to a decrease in the stability of the zircon with increasing alkalinity of the magma. Zircons from the Inchbae rock have not been isotopically disturbed since granite emplacement. On the other hand zircons from the finer-grained Lochan a' Chairn rock have been slightly disturbed and the riebeckite gneiss zircons have experienced a strong recent isotopic disturbance. This suggests a correlation between granite type and the stability of the zircon U–Pb isotopic systems, though the mechanism is not understood. The stability of the Rb–Sr whole-rock systems can also be correlated with rock type. Whereas the Inchbae and Lochan a' Chairn rocks have not been isotopically disturbed since granite emplacement the Rb–Sr whole-rock systems of the riebeckite gneiss were strongly disturbed ca. 425 m.y. ago.

1. Introduction

The presence of excess radiogenic lead in zircons from intrusive granites has been reported by a number of authors (e.g. [1–3]). This paper reports a similar occurrence in zircons from the pre-Caledonian Carn Chuinneag granite of the Scottish Highlands and considers the implications of these isotopic results on the origin of the granite and the stability of zircons in the granite magma. We also report evidence on the comparative behaviour of zircon U–Pb and whole-rock Rb–Sr systems for three phases of the granite complex in response to a common post-emplacement geological history.

2. Geological setting

The Carn Chuinneag granite (Fig. 1) was emplaced in the Moine sediments of northern Scotland before the onset of the Caledonian orogeny. The granite distended the Moine cover and metamorphosed the surrounding sediments to a distance of 1–1.5 km [4, 5].

The Carn Chuinneag granite is composed of several distinct units [4, 5]. Three of these were investigated in this study: a coarse-grained gneissic granite called the *Inchbae rock*, a finer-grained gneissic granite called the *Lochan a' Chairn rock* and a *riebeckite-bearing gneissic* granite [6]. Harker [6] concluded that the

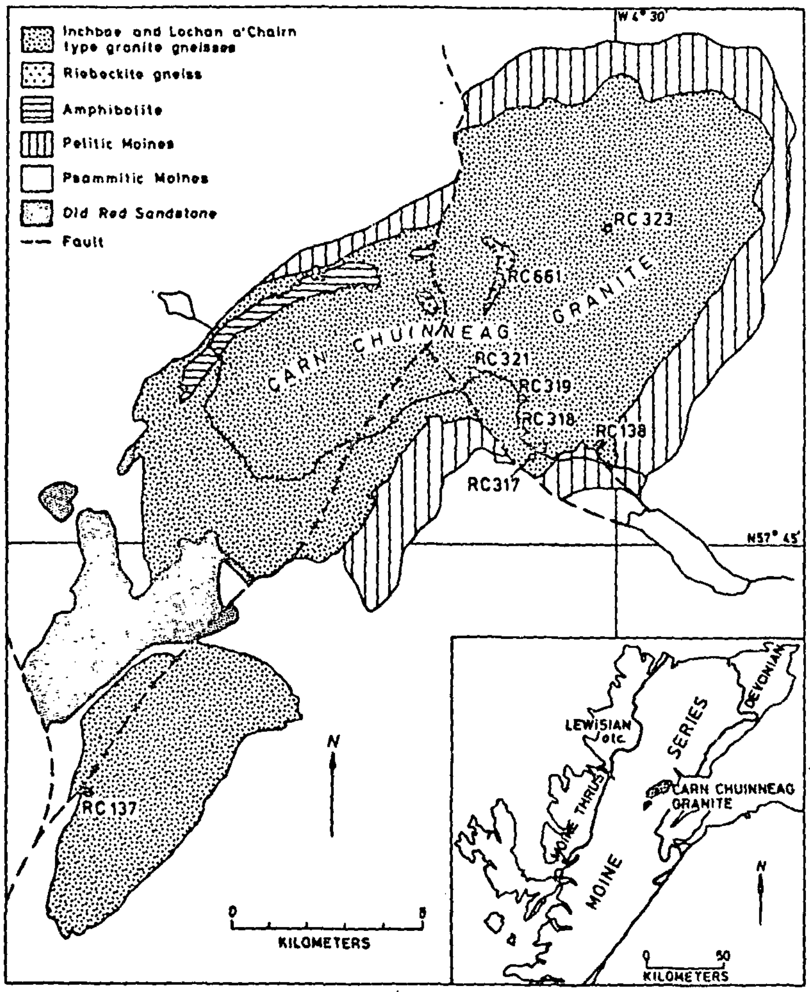

Fig. 1. Geological sketch map of the Carn Chuinneag granite showing sample locations (from the 1-inch to 1-mile Alness sheet of the Geological Survey).

Lochan a' Chairn rock was emplaced after the Inchbae rock. The intrusive relationships of the riebeckite gneiss are not known. The complex was metamorphosed to amphibolite facies during and after the second episode of Caledonian deformation that affected the surrounding Moines [4]. Long [7] and Long and Lambert [8] reported a Rb–Sr whole-rock isochron age for the Lochan a' Chairn and Inchbae phases of the Carn Chuinneag granite of 560 ± 10 m.y.[1] (initial $^{87}Sr/^{86}Sr$ = 0.710 ± 0.002), and interpreted this as the age of emplacement. A Rb–Sr mineral isochron, from a sample of Lochan a' Chairn rock, gave 412 ± m.y. with an intital $^{87}Sr/^{86}Sr$ of 0.782 ± 0.030. Long interpreted this isochron as indicating complete homogenisation of Sr isotopes among the minerals of the rock during a late Caledonian metamorphism which did not disturb the Rb–Sr whole-rock systems.

Long [7] also reported a single Rb–Sr whole-rock analysis of the riebeckite gneiss (sample 20529, Table 1). This highly alkalic rock has a $^{87}Rb/^{86}Sr$ of 151 and a maximum age (assumed initial $^{87}Sr/^{86}Sr$ = 0.700) of

[1] Rb–Sr ages are calculated with a ^{87}Rb decay constant of 1.39×10^{-11} yr^{-1}.

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TABLE 1
Rb–Sr whole-rock

Sample	Rb (ppm
Inchbae rock	
20784[3]	152
	151
RC 318	128.0
	124.3
RC 319	131.4
RC 321	136.7
RC 322	106.4
	104.6
Lochan a' Chairn roc	
20805[3]	264
20806[3]	249
20782[3]	243
Riebeckite gneiss	
20529[3]	164
	169
RC 661A	271.9
	275.6
RC 661D	138.9

[1] Normalized to $^{86}Sr/$
[2] Assumed initial $^{87}Sr/$
λ $^{87}Rb = 1.39 \times 10^{-1}$
[3] Analyses from Long

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rock is significantly y
Additional Rb–Sr
the Inchbae rock and
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the Inchbae whole-roc
granite isochron [7], v
Lochan a' Chairn data
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this body of 425 ± 15
0.710) (Table 1).
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metamorphism [4], wl
gneiss, can not be olde
flicts with the conclusi
that the metamorphis

TABLE 1
Rb–Sr whole-rock analyses

Sample	Rb (ppm)	Sr total (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr$ [1]	Age [2] (m.y.)
Inchbae rock					
207843 [3]	152	183	2.41	0.7316	
	151	192	2.27	0.7296	
RC 318	128.0	212.6	1.746	0.7239	
	124.3	206.3	1.748	0.7244	
RC 319	131.4	147.3	2.589	0.7305	
RC 321	136.7	141.0	2.812	0.7317	
RC 322	106.4	140.3	2.200	0.7251	
	104.6	143.3	2.117	0.7253	
Lochan a' Chairn rock					
208053 [3]	264	34.3	22.27	0.8841	
208063 [3]	249	46.4	15.53	0.8309	
207823 [3]	243	23.3	30.14	0.9487	
Riebeckite gneiss					
205293 [3]	164	3.2	150.7	1.644	444
	169	2.6	186.8	1.823	427
RC 661A	271.9	2.71	348.9	2.794	428
	275.6	2.70	357.0	2.838	427
RC 661D	138.9	2.08	216.0	1.930	405

[1] Normalized to $^{86}Sr/^{88}Sr = 0.1194$.
[2] Assumed initial $^{87}Sr/^{86}Sr = 0.710$. Ages calculated using λ $^{87}Rb = 1.39 \times 10^{-11}$ yr^{-1}.
[3] Analyses from Long [7].

430 ± 5 m.y. He interpreted this as the age of emplacement of the riebeckite gneiss, concluding that this rock is significantly younger than the main intrusion.

Additional Rb–Sr whole-rock measurements of the Inchbae rock and the riebeckite gneiss are reported in Table 1. The new results confirm the location of the Inchbae whole-rock points on the Carn Chuinneag granite isochron [7], which is controlled by the three Lochan a' Chairn data points, but they do not add to the precision of this isochron. New analyses of the riebeckite gneiss confirm a Rb–Sr whole-rock age for this body of 425 ± 15 m.y. (assumed intial $^{87}Sr/^{86}Sr$ = 0.710) (Table 1).

On this evidence the D2–D3 amphibolite facies metamorphism [4], which affected the riebeckite gneiss, can not be older than 425 ± 15 m.y. This conflicts with the conclusions of Van Breemen et al. [9] that the metamorphism must be older than 450 m.y.

3. The investigated rock types and their zircons

3.1. *Inchbae rock*

This is a coarse-grained, biotite-bearing, gneissic granite. Phenocrysts are generally composed of orthoclase in various stages of inversion to microcline, depending on the extent of the main D2 foliation [4, 6]. Plagioclase, mostly oligoclase, also occurs as phenocrysts but is more common in the groundmass. Some plagioclase is zoned and is generally cloudy in contrast to clear K-feldspar [6]. The groundmass generally consists of a mosaic of equidimensional granoblastic quartz and K-feldspar. Biotite occurs as small oriented laths in recrystallised rock or as large random laths in less altered areas. Chloritisation of biotite and exsolution of iron oxide suggest chlorite-grade metamorphic retrogression. Accessory minerals include garnet, epidote, sphene, iron ore, zircon and orthite. Zircon abundances are 300 ppm in sample RC 137, 70 ppm in RC 138 and 200 ppm in RC 317.

The zircons are pale hyacinth with length-to-breadth ratios (L/B) of 2–4 to 1. Generally crystal forms are well developed [10], though a number of grains are irregular. Following the classification of Pupin and Turco [11] common forms are S10, S12, P3 and P4. A number of crystals show concentric euhedral internal zones which are rarely transgressed by deep embayments. In the finer size fractions terminations are blunted and the zircons lose their sharp appearance. No definite evidence of late stage overgrowths was found. Grains contain a few unidentified irregular to round inclusions and rarely, bubbles and elongate holes. A few grains have cores of metamict zircon which are generally irregular, though some have well-developed terminations. The presence of fractures radiating from the cores into the host zircons indicates differential expansion due to greater metamictness of the zircon cores.

3.2. *Lochan a' Chairn rock*

This is a finer-grained gneissic granite of restricted occurrence [6]. Mineralogically it is similar to the Inchbae rock though the large K-feldspar phenocrysts are less abundant. The fine groundmass consists of quartz, feldspar and biotite. Accessory minerals are epidote, sphene, apatite, iron ore and zircon [6]. Zircon comprises 60 ppm of Lochan a' Chairn rock RC 323.

TABLE 2
U–Pb isotopic analyses of zircon

Size fraction (microns)		Pb (ppm)	U (ppm)	$^{206}Pb/^{204}Pb$	Atom percent radiogenic lead[1]			Atomic ratios		
					206	207	208	$^{207}Pb/^{206}Pb$	$^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$
Inchbae rock										
1. RC 137,	−142 + 106NM[2]	28.7	306	1710	87.00	5.267	7.733	0.06054	0.7911	0.0948
		30.1	323	2040	87.13	5.266	7.603	0.06043	0.7888	0.0947
2.	−106 + 84 NM	30.7	327	1980	87.02	5.235	7.743	0.06016	0.7899	0.0952
		30.5	328	1180	86.88	5.254	7.865	0.06047	0.7830	0.0939
3.	− 45 + 30 NM	38.6	418	2220	86.68	5.212	8.111	0.06013	0.7727	0.0932
4. RC 138,	+ 142 NM	31.3	296	1100	85.47	5.622	8.911	0.06578	0.9534	0.1051
5.	−142 + 106 NM	29.3	280	1260	85.57	5.489	8.937	0.06414	0.9195	0.1039
6.	− 84 + 61 NM	33.5	333	1845	85.90	5.425	8.671	0.06315	0.8751	0.1005
7.	− 61 + 42 NM	37.0	375	2885	86.28	5.403	8.312	0.06262	0.8546	0.0990
8.	− 61 + 42 M1[0]	64.2	697	2900	88.10	5.360	6.534	0.06084	0.7922	0.0944
9. RC 317,	−165 + 142 NM	31.7	315	1120	86.29	5.529	8.183	0.06407	0.8912	0.1009
		31.1	311	2425	86.26	5.530	8.214	0.06411	0.8882	0.1005
10.	−142 + 106 NM	33.1	339	1470	86.66	5.425	7.913	0.06260	0.8481	0.0982
11.	− 61 + 45 NM	39.7	429	1870	87.35	5.328	7.315	0.06100	0.7915	0.0941
12.	− 45 NM	39.4	421	2265	87.21	5.310	7.476	0.06088	0.7976	0.0950
Lochan a' Chairn rock										
13. RC 323,	+ 142 NM	56.4	594	1375	82.69	5.044	12.26	0.06100	0.7677	0.0913
14.	− 84 + 61 NM	70.3	747	1990	81.72	4.860	13.42	0.05946	0.7332	0.0894
15.	− 45 NM	73.1	791	3170	81.70	4.885	13.42	0.05979	0.7241	0.0878
		75.7	837	2640	81.83	4.851	13.32	0.05930	0.7030	0.0860
Riebeckite gneiss										
16. RC 661C,	−165 + 142 NM	37.1	446	995	79.33	4.624	16.04	0.05830	0.5343	0.0665
17.	−106 + 84 NM	30.8	456	1025	79.92	4.588	15.49	0.05740	0.4959	0.0627
18.	− 61 NM	36.2	422	1045	80.49	4.668	14.84	0.05799	0.6425	0.0804
19.	−165 + 142 M3[0]	66.0	716	544	71.04	4.091	24.87	0.05759	0.6038	0.0760
20.	− 84 + 61 M3[0]	68.4	738	275	75.33	4.307	20.36	0.05718	0.6389	0.0810
21. RC 661D,	−106 + 84 NM	29.5	344	1240	77.00	4.488	18.51	0.05829	0.6153	0.0766

[1] Common lead correction: $^{206}Pb/^{204}Pb = 18.1$, $^{207}Pb/^{204}Pb = 15.5$, $^{208}Pb/^{204}Pb = 36.5$. [2] NM = non-magnetic; M = slightly magnetic.

The zircons are pale hyacinth and generally cloudy with L/B ratios of 2–4 to 1. Forms are similar but much more irregular than zircons from the Inchbae rock. Concentric euhedral internal growth zones can be seen in comparatively clear grains. Irregular cores of cloudy zircon, forming foci for radiating fractures, are present in a number of grains. The distribution of unidentified irregular inclusions and elongate holes is similar to that in the Inchbae rock zircons which they resemble except for their higher percentage of irregular and cloudy grains.

3.3. Riebeckite gneiss

This medium- to fine-grained, strongly foliated rock [5, 6] of granulose texture is confined to two small outcrops (Fig. 1). It is composed of microline, albite-oligoclase, quartz, riebeckite, and a little aegerine. The riebeckite forms ragged prisms or poikilitic masses enclosing quartz and feldspar. Iron ore and zircon are the most common accessories. The zircon content of the riebeckite gneiss samples (RC 661C and RC 661D) is 500 ppm.

The zircons are cloudy with L/B ratios of 2.3 to 1. External forms are mostly irregular, much more so than in either the Lochan a' Chairn rock or Inchbae rock. A few comparatively clear grains show concentric euhedral zoning suggesting that the irregular forms resulted from late-stage surface corrosion. Grains contain randomly oriented needle- and rod-shaped inclusions and other unidentified irregular bodies. In one or two cases cores of zircon with associated radiating fractures were observed. Such cores are rare in comparison to the number in zircons from the Inchbae and Lochan a' Chairn rocks.

4. Zircon U–Pb results

Analytical results of zircon size and magnetic fractions are given in Table 2 and displayed on a concordia

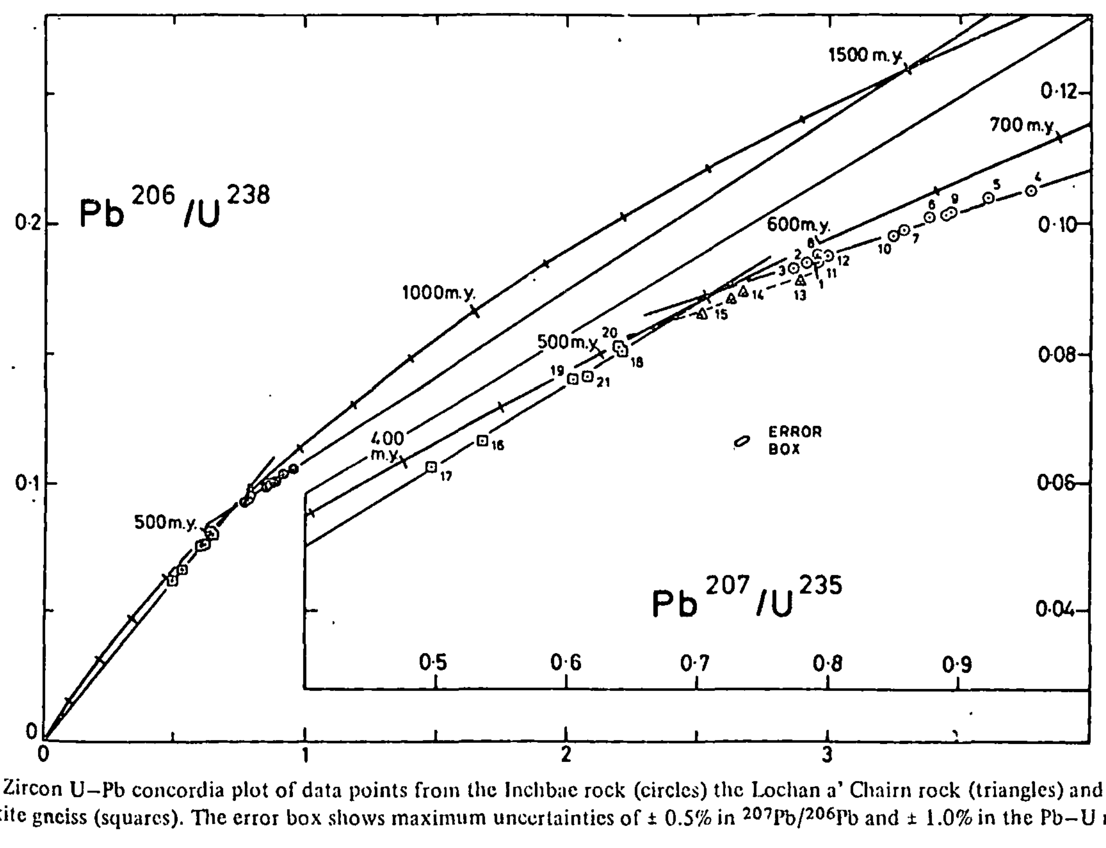

Fig. 2. Zircon U–Pb concordia plot of data points from the Inchbae rock (circles) the Lochan a' Chairn rock (triangles) and the riebeckite gneiss (squares). The error box shows maximum uncertainties of ± 0.5% in $^{207}Pb/^{206}Pb$ and ± 1.0% in the Pb–U ratios.

1 Common lead correction: $^{206}Pb/^{204}Pb$ = 18.1, $^{207}Pb/^{204}Pb$ = 15.5, $^{208}Pb/^{204}Pb$ = 36.5. 2 NM = non-magnetic; M = slightly magnetic.

plot in Fig. 2. Analytical methods are described by Van Breemen et al. [9][1].

4.1. Inchbae rock

Zircons from the Inchbae rock are exceedingly discordant. Twelve data points from three independent zircon populations (RC 317, RC 137, RC 138) define a single chord with a lower intersection with concordia of 560 ± 10 m.y. and an upper intersection of 1500 ± approximately 200 m.y. (this uncertainty is a visual estimate only).

4.2. Lochan a' Chairn rock

Zircons from the Lochan a' Chairn rock are also very discordant (Fig. 2). The three points from the single population fall beneath the Inchbae rock chord and are approximately aligned with a lower intersection with concordia at about 530 m.y.

4.3. Riebeckite gneiss

The riebeckite gneiss zircon points from two separate populations are discordant and fall close to a single chord with an upper intersection with concordia of 550 ± 20 m.y. and a lower intersection not significantly different from zero million years (Fig. 2).

5. The nature of the 560-m.y. event

The reality of the 560-m.y. old event is demonstrated by the lower intersection of the Inchbae rock zircon chord and concordia at 560 ± 10 m.y., the upper intersection of the riebeckite gneiss zircon chord and concordia at 550 ± 20 m.y. and the Rb–Sr whole-rock isochron age of the Lochan a' Chairn rock (and Inchbae rock) of 560 ± 10 m.y.

Long interpreted the 560-m.y. old event as the age of granite emplacement (of the Inchbae and Lochan a' Chairn rocks). An alternative explanation is that this age is recording the amphibolite facies metamorphism and that granite emplacement occurred around 1500 m.y. ago. We consider this to be most unlikely because zircons from *post*-tectonic Caledonian granites have similar discordance patterns with upper intersections with concordia in the order of 1600 m.y. and with lower intersections of around 400 m.y. recording the ages of emplacement (unpublished results of R.T.P.). We conclude, therefore, that 560 m.y. is the age of emplacement of the Carn Chuinneag granite, including the riebeckite gneiss, and the upper intersection age has some other significance.

6. Excess radiogenic lead in the zircons

It follows from the U–Pb isotopic relationship in Fig. 2 and the conclusion that granite emplacement occurred 560 ± 10 m.y. ago that zircons in the Inchbae rock (and to a lesser extend the Lochan a' Chairn rock) contain an initial component of radiogenic lead much older than the granite itself. This excess radiogenic lead cannot be simply rock lead incorporated in the crystallizing zircon. Rather it must be present in the zircon populations in a mineral phase, presumably zircon. Separate zircon xenocrysts have not been recognised; however, some of the zircon cores could be xenocrysts which survived in the magma to form nuclei about which subsequent zircon crystallized. Such xenocrysts could have come from the original source rocks or they could be from xenoliths stoped off the walls during emplacement. There is no evidence that a significant amount of metasediment has been incorporated into the granite magma during emplacement. Metasedimentary xenoliths are only evident near the contact. It is more likely that the inherited zircons are relicts of the original source rocks and as such are primary constituents of the magma.

The conclusion that the Inchbae granite zircons contain a component of zircon from the early source rocks raises the question of the geological significance of the "upper intersection age" of 1500 ± 200 m.y. Is this the age of the original granite source material or is it a spurious apparent age reflecting the method of subdividing a mixed zircon population [12]? The consistent fit of zircon data points from the three independent populations from the Inchbae rock to a single chord strongly suggests that the upper intersection age of 1500 ± 200 m.y. is geologically significant and we tentatively interpret this as the age of the source rocks. This is consistent with the high initial $^{87}Sr/^{86}Sr$ ratio of the Carn Chuinneag granite (0.710 ± 002).

[1] Constants used were $\lambda^{238}U = 1.53 \times 10^{-10}\ yr^{-1}$, $\lambda^{235}U = 9.72 \times 10^{-10}\ yr^{-1}$. $^{238}U/^{235}U = 137.8$.

Deep-lying Lewisian rocks could be considered as possible source rocks for the Carn Chuinneag granite. However zircons from Lewisian gneisses and granulites, although discordant, record Pb–Pb ages in the order of 2500–2700 m.y. [13–15]. Consequently it would appear unlikely that the inherited zircons in the Carn Chuinneag granite were derived from rocks of similar age to presently exposed Lewisian gneisses. Minor Laxfordian granites in the Lewisian gneisses have zircon ages of ca. 1700 m.y. [15]. These could be a surface expression of more extensive 1700-m.y. old basement beneath.

Whereas there is a significant component of excess radiogenic lead in zircons from the Inchbae rock and Lochan a' Chairn rock there is no indication of any excess radiogenic lead in zircons from the riebeckite gneiss (Fig. 2). One explanation of this is that the riebeckite gneiss magma never contained "old" zircon. A second explanation is that zircon xenocrysts were present in the riebeckite granite magma, but were completely dissolved prior to granite emplacement. We have no way of deciding between these explanations. The zircons from the Lochan a' Chairn rock appear to represent an in-between case as, although they clearly show a component of inherited radiogenic lead, this is less than that found in zircons from the Inchbae rock. This decrease in zircon xenocrysts with rock type could therefore be reflecting the mode of formation of final granite fractions, the xenocrysts being preferentially concentrated in the less fractionated rocks, or it could indicate the stability of zircon in the respective magmas. Under this explanation water content cannot be the main factor governing the zircon stability in the granite magma as, from the few chemical analyses available, the water content of the riebeckite gneiss appears to be less than that of the other two granite types [5, 6]. These analyses and unpublished partial chemical analyses by G. Angell of the University of Edinburgh show that sodium concentration increases from Inchbae rock, to Lochan a' Chairn rock, to riebeckite gneiss. The overall increase is only about 2–3%. Nevertheless, from previous conclusions on the instability of zircons in alkaline magmas [16, 17] and the relationships noted above, we would suspect that the pattern of survival of original zircon in the three granite phases could have depended on the alkalinity of the magma.

7. The post-emplacement stability of the isotopic systems

7.1. Zircon U–Pb systems

There has been no significant disturbance of the U–Pb systems of the Inchbae rock zircons since 560 ± 10 m.y. ago. On the other hand zircon U–Pb systems from the Lochan a' Chairn rock have undergone a slight post-emplacement isotopic disturbance resulting in a lower apparent "intersection age" of about 530 m.y. and zircons from riebeckite gneiss have experienced a strong recent isotopic disturbance. It is not known which event disturbed the Lochan a' Chairn zircons – the 425-m.y. old event registered by the Rb–Sr systems, the recent isotopic disturbance registered by the riebeckite gneiss zircons, or both.

The isotopic disturbance patterns, correlate well with granite type. As the uranium concentrations of zircon fractions from the three granite types overlap (Table 2) the discordance behaviour cannot be related to the relative radiation damage. Also it does not seem possible to explain these relationships by a mechanism of Pb loss by slow continuous diffusion as this implies a close relationship between the Pb diffusion constant in the zircons and granite type. The relationship of zircon discordance to rock type could possibly be explained in terms of episodic lead loss through the action of groundwater during uplift and dilation [18]. Such a model requires that groundwater action was significant in the riebeckite gneiss, minimal in the Lochan a' Chairn rock, and absent from the Inchbae rock. Such selectivity is difficult to accept. There is no indication of increased alteration of the feldspar in the riebeckite gneiss – rather the reverse. Also the $\delta^{18}O/^{16}O$, values for the Inchbae and riebeckite gneiss samples (RC 319, RC 661 D) of + 10 and + 12‰ (S.M.F. Sheppard, personal communication) argue against large-scale groundwater interaction. Further investigation is needed before we can adequately explain the apparent influence of granite type on the degree of post-emplacement isotopic disturbance of the zircon.

7.2. Rb–Sr whole-rock systems

The Rb–Sr whole-rock isochron of the Inchbae and Lochan a' Chairn biotite granites has not been disturbed since emplacement. Long [7] believed that the 425 ± 15 m.y. age for the riebeckite gneiss is the age of emplacement of the body, and that this rock has also remained isotopically undisturbed by post-emplacement events. However, if we accept the zircon age of 550 ± 20 m.y. as the true age of emplacement, it would appear more likely that the Rb–Sr whole-rock system of the riebeckite gneiss has undergone essentially complete re-equilibration or loss of radiogenic strontium 425 ± 15 m.y. ago. This demonstrates a lower stability of the Rb–Sr whole rock system of the riebeckite gneiss relative to the other granite types. Other examples of the instability of the whole-rock Rb–Sr systems of alkali-rich granites have been reported [19, 20]. We tentatively relate the strontium isotopic disturbance of the riebeckite gneiss (of maximum age of 430 m.y.) to the event which re-equilibrated the mineral Rb–Sr systems; however, we are not prepared at this stage to correlate the 425 ± 15 m.y. isotopic disturbance with one or other of the metamorphic and structural events recognised in the region. Unlike the zircon U–Pb systems from the riebeckite gneiss the Rb–Sr isotopic systems have not been affected by a recent isotopic disturbance.

Acknowledgements

We would like to thank Dr. R.M. Macintyre, Dr. L.E. Long and Dr. R. St. J. Lambert for commenting on the manuscript and Professor H.W. Wilson for his interest in the work. Dr. M. Aftalion, Dr. O. van Breemen, Mr. J. Jocelyn and Mr. J. Hutchison assisted with the analytical work. The Isotope Geology Unit of the Scottish Universities Research and Reactor Centre is supported by the Geology Departments of the Universities of Scotland and N.E.R.C. Research Grant.

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[AMERICAN JOURNAL OF SCIENCE, VOL. 277, FEBRUARY, 1977, P. 136-177]

$^{18}O/^{16}O$, D/H, AND $^{13}C/^{12}C$ STUDIES OF THE TERTIARY IGNEOUS COMPLEX OF SKYE, SCOTLAND†

RICHARD W. FORESTER* and HUGH P. TAYLOR, JR.**

ABSTRACT. In southern Skye, $\delta^{18}O$ analyses of 350 samples show that almost all the rocks within 4 km of the central intrusive complexes are depleted in ^{18}O due to extensive interaction with heated meteoric ground waters. Because of higher permeabilities, the plateau lavas are most widely affected (outward to 8 km). Whole-rock $\delta^{18}O$ values (SMOW) of basalts (−7.1 to +8.4), Mesozoic shales (−0.6 to +12.4), and Precambrian sandstones (−6.2 to +10.8) systematically decrease *inward* toward the center of the plutonic complex. In the Cuillin gabbro, $\delta^{18}O$ of plagioclase (−7.1 to +2.5) and pyroxene (−0.5 to +3.2) decrease outward toward the margins of the pluton. Most of these ^{18}O depletions were produced by subsolidus exchange, but it also appears that the original Cuillin gabbro magma was depleted in ^{18}O, with a $\delta^{18}O \cong +3.5$. The Red Hills epigranite plutons have $\delta^{18}O$ quartz (−2.7 to +7.6) and feldspar (−6.7 to +6.0) that suggest about 80 percent of the exchange took place at subsolidus temperatures; profound disequilibrium quartz-feldspar fractionations (up to 12.0) are characteristic. The early epigranites were, however, apparently intruded as low-^{18}O magmas (^{18}O depletions of up to 3 per mil), with $\delta^{18}O$ of quartz *decreasing* progressively with time. Successively later intrusions exhibit *increasing* $\delta^{18}O$ quartz, but a major $\delta^{18}O$ discontinuity is observed at the geologic break between intrusion of the granites of the Western and Eastern Red Hills. The Southern Porphyritic epigranite was intruded as a low-^{18}O magma with an extremely non-homogeneous $\delta^{18}O$ of −3.0 to +3.0, suggesting that it was formed by partial melting of hydrothermally altered country rocks at depth; a similar origin may apply to the Coire Uaigneich granophyre. A good correlation exists between grain size and $\delta^{18}O$ for the unique, relatively normal-^{18}O Beinn an Dubhaich granite, which intrudes limestone having a $\delta^{18}O$ range of +0.5 to +20.8 and $\delta^{13}C$ (PDB) of −4.9 to −1.0. The δD values (SMOW) of sericites (−104 to −107), and amphiboles, chlorites, and biotites (−105 to −128) from the igneous rocks are all low compared to "normal" igneous rocks, indicating that Eocene surface waters at Skye had $\delta D \cong -85$ and $\delta^{18}O \cong -12$. The average integrated water/rock ratio for the Skye hydrothermal system is approximately unity; at least 2000 km^3 of heated meteoric waters were cycled through these rocks.

INTRODUCTION

An oxygen isotope study of the Tertiary igneous rocks from Skye, Mull, and Ardnamurchan by Taylor (1968) and Taylor and Forester (1971) established the fact that large-scale exchange occurred between the epizonal plutons and heated, low-^{18}O meteoric ground waters during Eocene igneous activity. This kind of interaction is now well documented from a wide variety of localities (Taylor, 1971, 1973, 1974b; Taylor and Forester, 1973; Sheppard and Taylor, 1974; O'Neil and others, 1973; Forester and Taylor, 1972, 1974), but the details of this process are still being worked out. For example, we would like to determine (1) whether or not the silicate melts themselves were contaminated with meteoric waters, or whether the interaction took place entirely with already solidified rocks; (2) the effect of the type of country rock on the extent and amount of isotopic exchange, and (3) the effect of grain size and rock structure on the hydrothermal exchange process. In order to attempt to

† Contribution No. 2701, Publication of the Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125

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/^{12}C STUDIES
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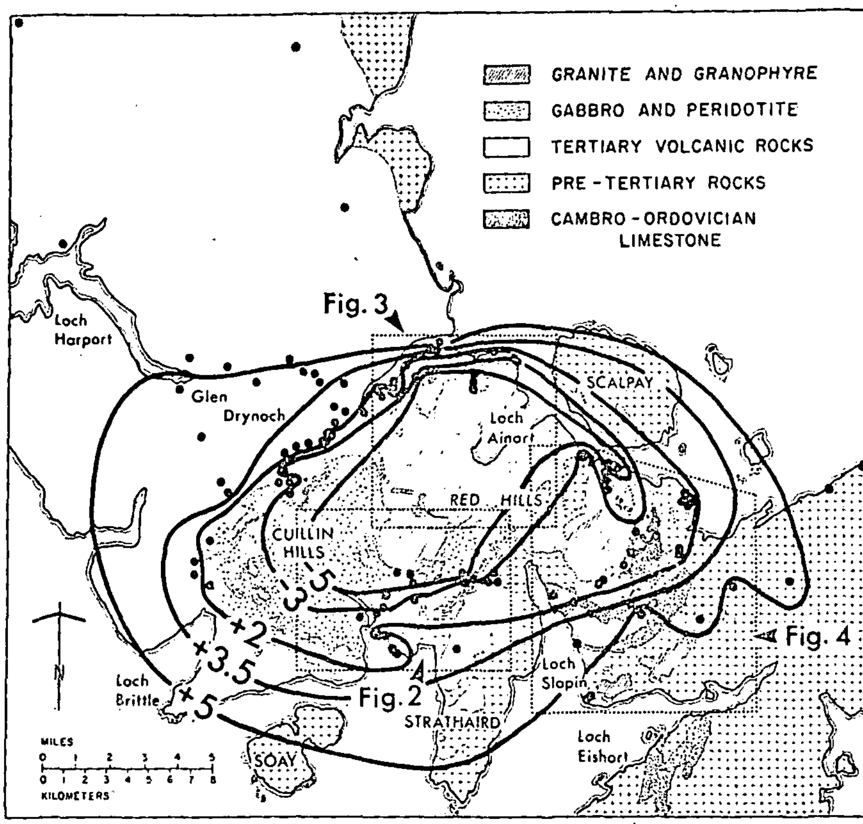

Fig. 1. Contours of whole-rock δ^{18}O values for basalts, agglomerates, tuffs, and pre-Red Hills basaltic dikes. δ^{18}O contours are drawn at +5, +3.5, +2, —3, and —5, in order to indicate the hydrothermal changes that have occurred in these rock types, all of which have basically similar grain size and mineralogy. Black dots are sample localities. The rectangular areas outlined by dashed lines are the regions shown in figures 2, 3, and 4.

answer these and other questions, a detailed sampling program was undertaken at Skye, which appeared to be the most promising of the low-^{18}O complexes studied by Taylor and Forester (1971). This paper presents the ^{18}O/^{16}O, D/H, and ^{13}C/^{12}C analyses obtained as a result of that sampling program.

The Tertiary geology of southern Skye was first mapped in detail by Harker (1904). Richey (1961) and Brown (1969) have given summary accounts of the Tertiary igneous rocks of Skye, and a description of the entire Scottish Hebridean region has also been published by Stewart (1965). A generalized geologic map of the area is shown in figure 1.

All the ^{18}O/^{16}O and ^{13}C/^{12}C ratios of rocks and minerals in the present study are given in the appendix[1] together with brief descriptions

[1] For complete set of data, order NAPS Document 02954 from ASIS/NAPS, c/o Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, N.Y. 10017; remitting $3.00 for microfiche or $5.50 for each photocopy. Outside the United States and Canada postage is $3.00 for a photocopy or $1.50 for a fiche.

of each rock. Table 1 gives all the D/H ratios. The $\delta^{18}O$ values from the central intrusive complexes are shown on geologic maps in figures 2, 3, and 4.

Most of the oxygen extractions from silicates and oxides were performed using the technique of Taylor and Epstein (1962a); some samples, however, were reacted with BrF_5 according to the method of Clayton and Mayeda (1963). Carbonates were reacted according to the method of McCrea (1950) and Epstein, Graf, and Degens (1963). Hydrogen was extracted utilizing a technique similar to that of Friedman (1953) and Godfrey (1962).

All isotopic analyses in this paper are given in the familiar δ-notation; the $\delta^{18}O$ and δD values are given relative to SMOW (Craig, 1961), while the $\delta^{13}C$ values are with respect to the PDB standard (Urey and others, 1951). The fractionation of isotopes between two phases Q and F is given by $\Delta_{Q\text{-}F} = 1000 \ln \alpha_{Q\text{-}F}$, where $\alpha_{Q\text{-}F}$ is the fractionation factor. Abbreviations used in this paper are as follows: Q = quartz, F = plagioclase, K = K-feldspar, P = clinopyroxene, M = magnetite, Ol = olivine, C = calcite, D = dolomite, W = H_2O, R = whole rock.

In the discussion that follows, we shall commonly refer to the concept of low-^{18}O igneous rocks or magmas. Application of this term implies

TABLE 1

Hydrogen isotopic analyses from Isle of Skye, Scotland

Sample (SK-)	Mineral*	Rock unit	δD** (per mil)	Remarks***
239D	Ep	Basalt	−38±0 (2)	
22	S	Felsite sheet	−104	
74	S	Allt Fearna Granite	−106	
225	S	Felsite dike	−107	
51	A	Broadford gabbro	−123	
99	A	Lewisian	−74	
189	A	Beinn an Dubhaich Granite	−120	
124	A	Glamaig Epigranite	−128±1 (2)	
219	A	Cuillin gabbro	−119	
173	A	Marsco Epigranite	−127	
177	A	Marsco Epigranite	−121±1 (2)	
521	A	Meall Buidhe Epigranite	−127	
532B	A+C	Basaltic dike	−105	50%A, 50%C
99	B	Lewisian	−72	
268B	B	Granitic dike	−118	
236C	C	Basalt	−122	
253B	C	Cuillin gabbro	−126	
243B	C	Basalt	−132	C amygdules
288	C+W	Torridonian sandstone	−101	70%C, 30%W, trace of Ep
90	W+C	Torridonian sandstone	−95	90%W, 10%C
88	W+C	Torridonian sandstone	−63	85%W, 15%C
89	W	Torridonian sandstone	−66	

* S = sericite; A = amphibole; C = chlorite; W = white mica; Ep = epidote.

** Analytical error is average deviation from the mean. Numbers in parentheses indicate number of separate analyses.

*** Complete description given in appendix. Mineral percentages give the estimated % contribution of each mineral to the measured δD value.

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δD** (per mil)	Remarks***
−38±0 (2)	
−104	
−106	
−107	
−123	
−74	
−120	
−128±1 (2)	
−119	
−127	
−121±1 (2)	
−127	
−105	50%A, 50%C
−72	
−118	
−122	
−126	
−132	C amygdules
−101	70%C, 30%W, trace of Ep
−95	90%W, 10%C
−63	85%W, 15%C
−66	

W = white mica; Ep = epidote.
the mean. Numbers in parentheses

Mineral percentages give the esti-
red δD value.

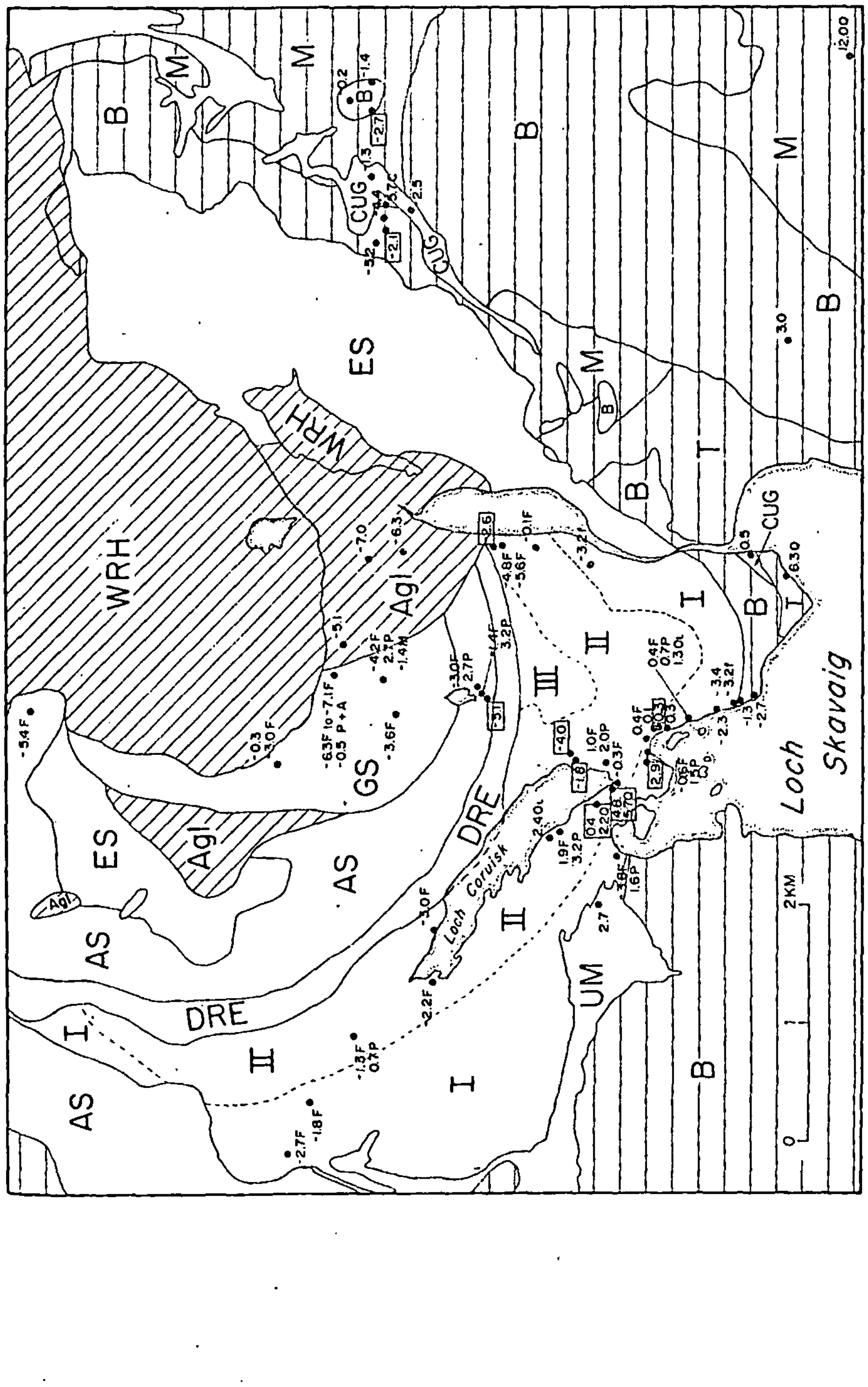

Fig. 2. Generalized geologic map (after Harker, 1904; and Wager and Brown, 1967), of that part of the Isle of Skye that includes the Cuillin gabbro and the Coire Ngaigneich granophyre (CUG), showing $\delta^{18}O$ values of plagioclase (F), pyroxene (P), olivine (Ol), magnetite (M), calcite (C), amphibole (A), quartz (Q), plagioclase phenocysts (f), and whole rock (no symbol). The $\delta^{18}O$ values obtained on dike rocks are enclosed in rectangles. ES = eucrite series; DRE = Druim nan Raunh eucrite; UM = ultramafic rocks; I, II, III = Zones I, II, and III of eucrite series; AS = allivalite series; GS = gabbro series. The diagonal lined pattern indicates later intrusions: Agl = agglomerate and tuff; WRH = Western Red Hills granites. The horizontal lined pattern indicates older country rocks: B = basaltic plateau lavas and outer gabbros; T = Torridonian; M = Mezozoic.

that a given igneous rock or silicate melt has a $\delta^{18}O$ value significantly lower than the "normal" range observed in similar types of igneous rocks throughout the rest of the world. The remarkable uniformity of $\delta^{18}O$ in most igneous rocks allows us to define a set of "normal" $\delta^{18}O$ values (Taylor, 1968) as a reference against which we can discern secondary changes in $\delta^{18}O$ that might have later been imposed upon a rock or magma. For example, if we exclude localities that have undergone the kind of meteoric-hydrothermal phenomena discussed in the present paper,

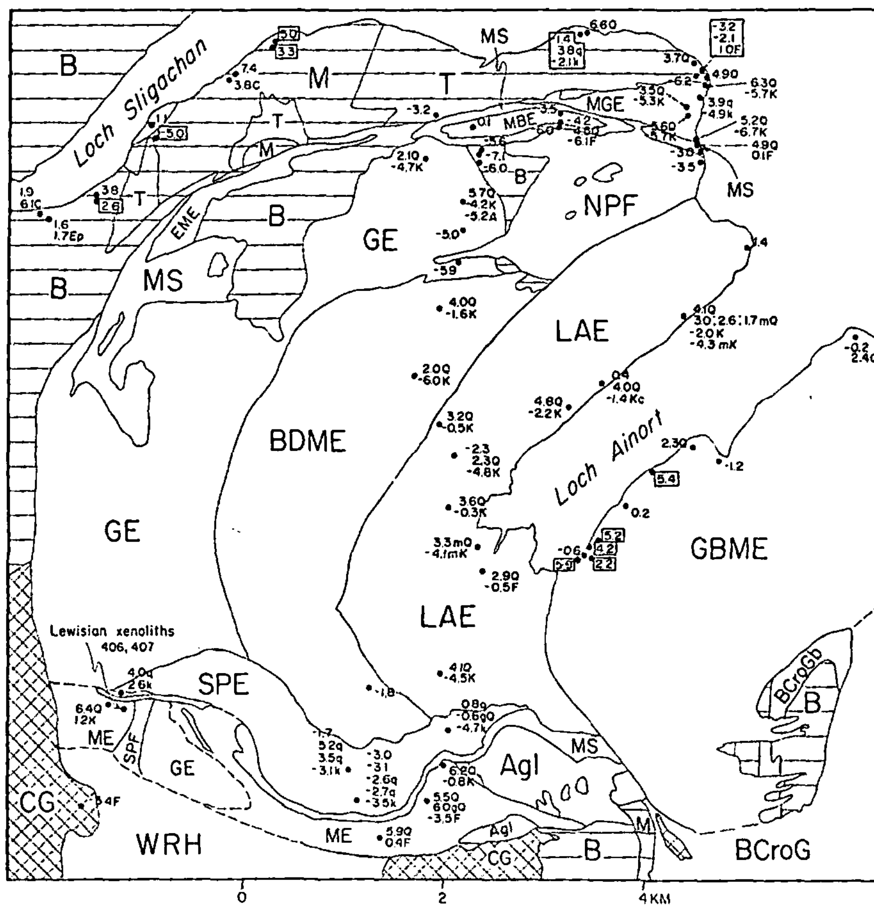

Fig. 3. Generalized geologic map of the Western Red Hills, Skye, showing $\delta^{18}O$ values obtained on the granites, dike rocks, and country rocks. K = K-feldspar, k = K-feldspar phenocrysts, q = quartz phenocrysts, Ep = epidote, m = miarolitic, c = calculated, g = granophyric; other symbols are in figure 2. Horizontal lined pattern indicates country rocks: B= basaltic plateau lavas; M = Mesozoic; T = Torridonian. MGE = Maol na Gainmhich epigranite; GE = Glamaig epigranite; BDME = Beinn Dearg Mhor epigranite; LAE = Loch Ainort epigranite; NPF and SPF = Northern and Southern Porphyritic felsites, respectively; SPE = Southern Porphyritic epigranite; MS = Marscoite suite; MBE = Meall Buidhe epigranite; ME = Marsco epigranite; Agl = agglomerate; CG = Cuillin gabbro; GBME = Glas Beinn Mhor epigranite; BCroGb = Beinn na Cro gabbro; BCroG = Beinn na Cro granite, EME = Eas Mor epigranite; WRH = undifferentiated granite.

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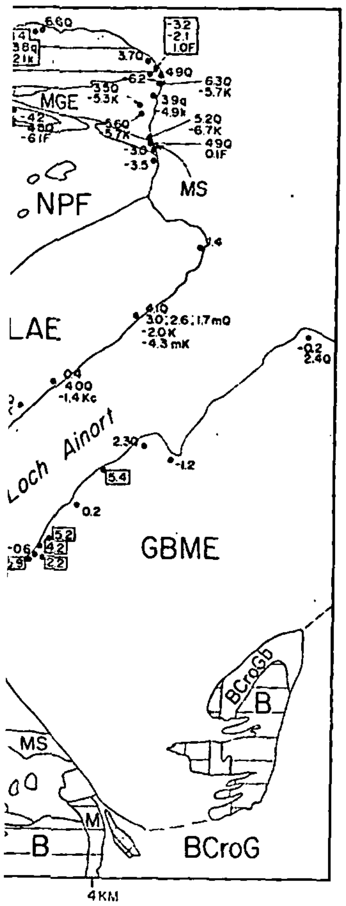

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2. Horizontal lined pattern indi-
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or epigranite; BCroGb = Beinn
E = Eas Mor epigranite; WRH

essentially all fresh basaltic or andesitic igneous rocks on the Earth and Moon have $\delta^{18}O = +5.5$ to $+7.0$, whereas granitic igneous rocks are more variable but typically have $\delta^{18}O = +7$ to $+10$ (Taylor, 1968; 1974a). Most igneous rocks with such "normal" $\delta^{18}O$ values also have relatively restricted ranges of δD as well, typically -50 to -85. Rocks with lower δD values are commonly found only in areas that also exhibit low $\delta^{18}O$ values; such low δD values are thus also attributed, in general, to exchange with heated meteoric waters (see Taylor, 1974a).

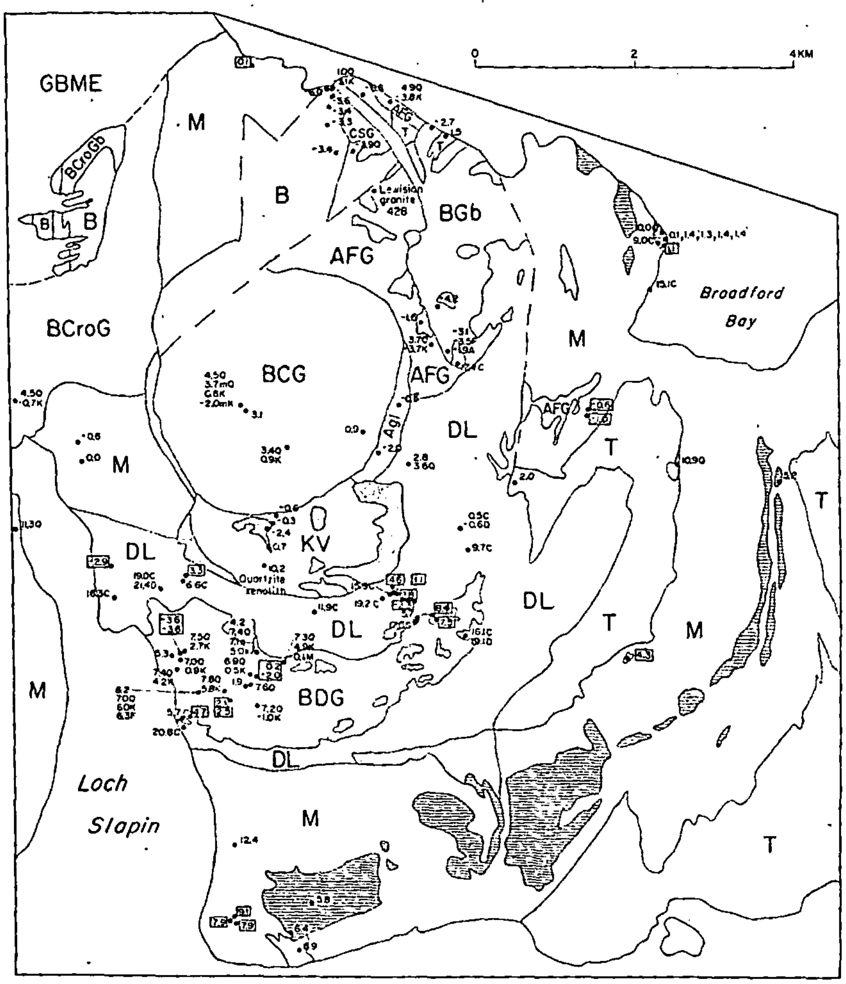

Fig. 4. Generalized geologic map of the Eastern Red Hills, Skye, showing $\delta^{18}O$ values obtained on the granites, dike rocks, and country rocks. Symbols as in figures 2 and 3. BCG = Beinn na Caillich granophyre; KV = Kilchrist vent and hybrids (stippled); BDG = Beinn an Dubhaich granite; AFG = Allt Fearna granite; BCroG = Beinn na Cro granite; BGb = Broadford gabbro; GBME = Glas Beinn Mhor epigranite; Agl = agglomerate and tuff; B = basaltic plateau lavas; M = Mesozoic; DL = Durness limestone; T = Torridonian; BCroGb = Beinn na Cro gabbro; CSG = Creag Strollamus granite. The horizontal striped pattern indicates the outer composite dolerite sills.

HYDROGEN ISOTOPE SYSTEMATICS

Hydrogen isotope analyses have been carried out on sericites, amphiboles, chlorites, biotites, and epidote from the Tertiary igneous rocks of Skye, as well as on several whole-rock samples from the Torridonian and Lewisian (table 1 and fig. 5). As in other areas where $\delta^{18}O$ analyses indicate that the igneous rocks have exchanged with heated meteoric waters, the D/H analyses at Skye confirm this effect (see also Taylor and Epstein, 1969).

The hydrogen isotope systematics exhibited by the igneous rocks at Skye are similar to those displayed by the rocks of the Skaergaard intrusion (Taylor and Forester, 1973) and the Stony Mountain complex, Colo. (Forester and Taylor, in preparation). Sericites are found to concentrate deuterium relative to the hydrous mafic silicates, but all the minerals are drastically lowered in δD with respect to "normal" igneous rocks (on the order of 50 per mil, see fig. 5). The sericites are very uniform in δD, with values of −104, −106, and −107. The chlorites have an average $\delta D = -127$ and are indistinguishable from the Tertiary amphiboles which average −124 (excluding SK-532B). The fact that hydrogen isotope fractionation depends on, among other things, the type of cation to which the OH^- is bonded (Suzuoki and Epstein, 1976) may account for why these Fe-rich chlorites from Skye have less deuterium,

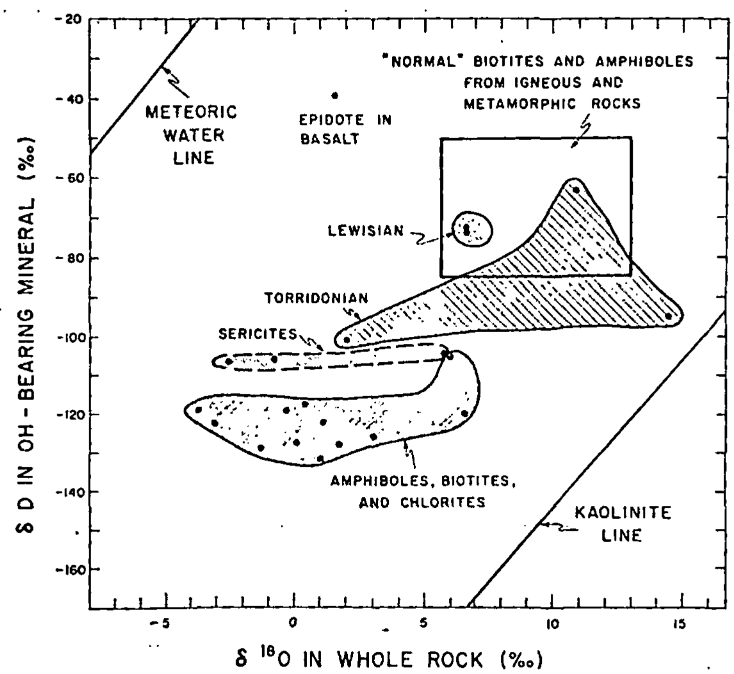

Fig. 5. δD-$\delta^{18}O$ diagram for hydroxyl-bearing minerals from Skye. The field of "normal" biotites and amphiboles (see Taylor, 1974a) is also shown, along with the meteoric water line (Craig, 1961) and the kaolinite line (Savin and Epstein, 1970a).

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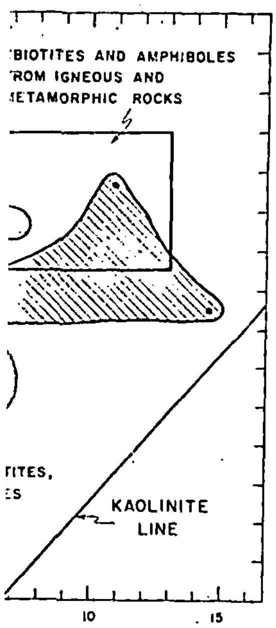

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relative to coexisting muscovite, than the high-Al chlorites from pelitic schists studied by Taylor and Epstein (1966).

The Tertiary amphibole with the most positive δD value (−105) is from SK-532B, which has a "normal" $\delta^{18}O_R = +5.9$, and is one of a series of basaltic dikes cutting the Glas Beinn Mhor epigranite on the southeast side of Loch Ainort that have relatively normal $\delta^{18}O$ (+5.2, +5.4, +4.2; see fig. 3). This is one of the few localities on Skye where there is evidence that some late-stage igneous activity occurred well after the emplacement of the major plutons, after the large meteoric-hydrothermal convection systems had been "turned off". The hydrothermal activity in the vicinity of the epigranite must have essentially ceased at the time of intrusion of these fine-grained dikes; otherwise the dikes would have exchanged with the meteoric-hydrothermal fluids and the adjacent low-^{18}O granophyric country rocks and thereby attained $\delta^{18}O \cong 0$ and $\delta D = -125$. The $\delta D = -105$ may represent mixing between small amounts of meteoric water and magmatic water from the dike, possibly as a result of partial hydrogen isotopic exchange with the surrounding epigranite.

Another interesting sample is the amphibole from SK-189, with $\delta D = -120$. This sample of Beinn an Dubhaich granite has the highest (most "normal") $\delta^{18}O$ values of quartz (+7.8) and alkali feldspar (+5.8) found in that pluton (see fig. 4), which is the least altered granite yet analyzed from Skye in terms of oxygen isotopes. In terms of D/H however, it is indistinguishable from rocks that have undergone drastic ^{18}O depletion. This is not unexpected, of course, because $\Delta^{18}O_{Q-K}$ is *slightly* larger than normal, suggesting some ^{18}O depletion of the alkali feldspar; note that inasmuch as the original H contents of these rocks are very low relative to their O contents, if the oxygen isotopic compositions have been measurably affected, one would expect that the original magmatic hydrogen isotopic record would be totally wiped out. This has apparently happened to all the analyzed Tertiary igneous rocks at Skye except for the aforementioned late-stage dikes that cut the Glas Beinn Mhor epigranite.

Data from the Torridonian are more difficult to interpret, because certain of the Torridonian rocks are composed of newly formed Tertiary alteration minerals, as well as Precambrian clastic and authigenic material. SK-288 is the only analyzed Torridonian sample collected close to the central intrusive complex, and it has clearly undergone significant oxygen isotope exchange ($\delta^{18}O_R = +2.0$). Its position on the δD versus $\delta^{18}O$ plot (fig. 5) is also indistinguishable from the Tertiary rocks whose dominant hydrous phase is sericite.

Both SK-88 (sandstone) and SK-89 (shale) have similar δD values (−63 and −66) that are much higher than any of the Tertiary samples except epidote from SK-239D. These samples are more than 8 km from the central intrusive center of Skye, well outside the area of hydrothermal alteration (see fig. 1). However, SK-90 is even further removed from the Tertiary plutonic complexes, approximately 12 km distant, yet it has an even lower $\delta D = -95$. The dominant hydrous phase in all three samples is white mica, but SK-90 is from a different group within the Torridonian succession. The SK-90 analyses plot very close to the kaolinite line on a $\delta D - \delta^{18}O$ graph (fig. 5); hence this sample conceivably could have undergone exchange with meteoric waters at very low temperatures.

Coexisting biotite and amphibole from a Lewisian schist (SK-99) have identical δD values of -73 ± 1. On the δD versus $\delta^{18}O$ plot of figure 5, the Lewisian samples fall within the area of "normal" isotopic values in igneous and metamorphic rocks, and thus these samples were apparently unaffected by the Tertiary events on Skye. This is not surprising, inasmuch as these samples are from outcrops more than 16 km away from the Tertiary plutonic centers.

The most enigmatic sample is SK-239D, an epidote with $\delta D = -38$ and $\delta^{18}O = +1.7$. This epidote is even more enriched in deuterium than biotites and amphiboles from "normal" igneous and metamorphic rocks. It is possible for the H_2O of a hydrothermal fluid to become enriched in deuterium, if it undergoes some reduction to H_2 or CH_4. However, a strongly reducing environment is not in accord with the presence of epidote, which is characterized by trivalent iron, nor with the estimated oxygen fugacities determined from the mineral assemblages in the altered rocks. Furthermore, it should be noted that a chlorite sample from a basalt only 1 km distant from SK-239D has a $\delta D = -122$.

No experimental work has been done on the D/H fractionations of epidote, and very few analyses have been reported. However, epidote-rich samples from the Boulder batholith, Mont. are richer in D than analogous epidote-poor samples (Sheppard and Taylor, 1974), and epidote amygdules from hydrothermally altered basalt surrounding the Skaergaard intrusion are about 20 per mil richer in deuterium than the chlorite amygdules (Taylor and Forester, 1973). These data suggest that at equilibrium epidote does in fact concentrate D relative to most other OH-bearing minerals, but the δD value of sample SK-239D is probably still too high to be explained by deposition from low-D meteoric waters. This sample therefore may represent a relict from an earlier, magmatic-hydrothermal alteration event that accompanied extrusion of the plateau basalts.

If we utilize a reasonable fractionation factor for the amphibole-water system using the data of Suzuoki and Epstein (1976), we can estimate that the Eocene meteoric-hydrothermal waters in Skye had $\delta D \cong -85$ to -90. Similarly, the sericite data suggest that the δD values of the hydrothermal fluids at Skye were approximately -85. Using the well-established relationship between δD and $\delta^{18}O$ in pristine meteoric waters (Craig, 1961), this gives $\delta^{18}O \cong -12$ for the early Tertiary meteoric surface waters on Skye. Because of the characteristic positive "^{18}O shift" shown by geothermal waters (Craig, 1963), this would represent the probable minimum value for all the Eocene meteoric hydrothermal waters at

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Skye; therefore all the oxygen isotope effects discussed below must have been produced by waters with $\delta^{18}O \geqslant -12$.

BASALTIC COUNTRY ROCKS AND DIKES

All sample localities representing basalts, vent agglomerates, tuffs, and those basaltic dikes intruded prior to the Red Hills granites are plotted on the regional geologic map in figure 1. The $\delta^{18}O$ contours in this figure are based on whole-rock $\delta^{18}O$ values measured on 111 samples of these rock types (see app). All these rocks are relatively fine-grained and have similar mineralogy; therefore they should all have offered approximately equal resistance to hydrothermal exchange. The late-stage basaltic dike rocks that cut the Red Hills granites are excluded because we want to monitor only the isotopic effects produced by hydrothermal alteration at the times of major plutonic activity.

The $\delta^{18}O_R$ values contoured in figure 1 are extremely systematic, decreasing inward toward the center of the plutonic complex. Essentially all the samples that lie outside the +5 contour have "normal" $\delta^{18}O$ values, but the centrally located samples inside the $\delta = -5$ contour must all have been depleted in ^{18}O by at least 10 per mil.

This radial inward depletion in ^{18}O is undoubtedly caused in part by increasing temperatures toward the intrusive centers (see meteoric-hydrothermal convection model of Taylor, 1971; and Taylor and Forester, 1971). If we assume that the overall, integrated water/rock (W/R) ratio was constant throughout the area of figure 1 during hydrothermal activity, we can assign approximate temperatures to each of the $\delta^{18}O$ contours (table 2). These calculations are based on an assumed initial $\delta^{18}O_{H_2O} = -12$, the value calculated from the hydrogen isotope data, and the W/R is based on atom percent oxygen in the water and rock. Note that for the types of rocks considered below, these calculated W/R ratios will be a factor of about 1.8 to 2.0 higher than the mass ratios of water to rock.

The assumption of constant W/R is obviously not entirely realistic. The actual W/R value probably increases inward toward the margins of the intrusives, because the flow of water is radially inward, and the rock volume decreases in the direction as the square of the distance (see Taylor, 1971; Norton, 1975). This type of increase of the W/R ratios in the vicinity of the heat source is also evident from the flow pattern analyses of Wooding (1957) and Elder (1965, 1967) and from measurements in modern geothermal systems, implying thermal gradients that are less steep, perhaps with values like those enclosed by the dashed lines in table 2. The simple closed-system model is also only an approximation. In the extreme open-system case, if the H_2O only makes a *single* pass through the rock before escaping from the system (that is, no convective cycling), then $(W/R)_{open} = \ln[(W/R)_{closed} + 1]$ and smaller W/R ratios are possible (see Taylor, 1976). On the other hand, the hydrothermal fluid will not always thoroughly equilibrate with the rocks, and the fluid also characteristically undergoes an ^{18}O shift; both processes act in a direction that counterbalances that of overestimating the W/R ratios, thus partially correcting the inherent errors in our simplified model.

Basalts SK-223 ($\delta^{18}O = -7.0$) and SK-518 ($\delta^{18}O = -7.1$) are the most ^{18}O-depleted whole-rock samples analyzed from Skye. It is impossible to explain these $\delta^{18}O$ values with initial $\delta^{18}O_{H_2O} > -6$. Even for $\delta^{18}O_{H_2O} = -9$, extremely high W/R ratios (>>10) would be required, if the temperatures were lower than 500°C. Thus the whole-rock $\delta^{18}O$ data *independently* tend to confirm the estimated initial $\delta^{18}O_{H_2O}$ value of about −12 calculated from the hydrogen isotope data. All basaltic whole-rock samples with $\delta^{18}O < -3$ require *minimum* W/R ratios of 1.0, and the average W/R ratio for these hydrothermally altered basalts had to be at least 0.5.

The $\delta^{18}O = +5$ contour represents the approximate outermost limit of meteoric-hydrothermal alteration in southern Skye. Essentially *all* the rocks within this area (~ 500 km²) are significantly depleted in ^{18}O. If the effects originally extended over a vertical distance of about 4 km, this implies that about 2000 km³ of rock have undergone appreciable ^{18}O-depletion, and therefore an approximately equal volume of water has passed through the rocks. This large amount of water can easily be ac-

TABLE 2

Calculated temperatures (°C)* of oxygen isotope exchange between H_2O and basaltic country rocks and dikes, assuming closed-system convective circulation, constant water/rock ratios, and isotopic equilibrium (because of more complete equilibration at higher temperatures, and because of radial inward flow of ground water toward the central complex, the effective W/R ratios must increase inward; a realistic gradient might be given by the values enclosed by the dashed lines).

	Temperature, °C					
δ_{Rf}	W/R = 0.5	W/R = 0.7	W/R = 1.0	W/R = 1.5	W/R = 2.0	W/R = 3.0
+5	105°	95°	85°	85°	85°	80°
+3.5	165°	140°	115°	110°	105°	100°
+2	270°	200°	160°	145°	135°	125°
0	710°	360°	240°	200°	180°	160°
−3	∞	∞	565°	360°	295°	245°
−5	∞	∞	∞	655°	450°	335°
−7	∞	∞	∞	∞	900°	510°

* Assuming $\delta_{Rf} = \delta_{F(An_{30})}$, utilizing the following equation (i = initial values, f = final values):

$$\frac{W}{R} = \frac{+6.5 - \delta_{Rf}}{\delta_{Rf} - [\Delta - 12]}$$

where

$+6.5 = \delta_{Ri}$, $\delta_{Wi} = -12$

and

$\Delta = 2.53\ (10^6\ T^{-2}) - 3.61$; T is in °K (O'Neil and Taylor, 1967).

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°C		
= 1.5	W/R = 2.0	W/R = 3.0
85°	85°	80°
10°	105°	100°
45°	135°	125°
00°	180°	160°
60°	295°	245°
55°	450°	335°
∞	900°	510°

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and Taylor, 1967).

counted for by normal amounts of rainfall. For example, with a catch basin area of 2000 km^2 and assuming that only 10 percent of an annual rainfall of 75 cm is added to the deep circulation system, it would require only 10^4 yr to supply the needed amounts of H_2O. It is certain that the intrusive igneous activity at Skye extended over a much longer period than this. Beckinsale (1974), for example, suggested that the igneous activity in Mull lasted for about 10 m.y.

The only basic problem, therefore, is accounting for the huge quantities of heat energy necessary to drive such large convection systems. If the hydrothermally altered rocks have been produced by an average rise in temperature of the basaltic country rocks from about 50° to 300°C, then with a specific heat of 0.25 cal/g /°C, 65 cal/g of heat must be added throughout the alteration zone. With $W/R \approx 0.6$, at least 0.3 g of H_2O must be heated along with every gram of rock, demanding an additional 85 cal/g. Thus the hydrothermal alteration process probably requires at least 150 cal/g. The maximum heat that can be liberated from a silicate melt crystallizing and cooling from 1000° to 300°C is about 280 cal/g. Exothermic hydration reactions in the country rocks may account for an additional 35 cal/g. Thus a cylindrical stock of magma contains only enough energy to produce a hydrothermally altered aureole about 0.7 stock diameters wide (see Taylor, 1971; 1794a). This calculated value is very close to what is actually observed in Skye (fig. 1), if the central intrusions are treated as a single, composite stock.

PRE-TERTIARY COUNTRY ROCKS

Lewisian gneiss.—The Precambrian Lewisian gneiss is important with regard to the present study because Moorbath and Bell (1965) have obtained $^{87}Sr/^{86}Sr$ data suggesting that the Tertiary granites of Skye formed by partial melting of the Lewisian basement. Therefore, several Lewisian basement gneiss samples from the area bordering the Sound of Sleat were analyzed. Three samples of these metamorphic rocks have $\delta^{18}O$ values of +6.0, +6.6, and +7.6. A 3 m-thick quartz vein within the Lewisian (SK-98) has a $\delta^{18}O = +9.4$. These samples are all more than 16 km from the central intrusive complex, at a distance where even the basalts would not have been affected (see fig. 1). It is also clear from the hydrogen isotopic analyses (fig. 5) that these Lewisian samples have not exchanged with Tertiary meteoric waters. Furthermore, the Tertiary dike rocks cutting the Lewisian all have normal $\delta^{18}O_R$ values (SK-93, 94, and 100 are +5.8, +6.0, and +7.0 respectively).

The Lewisian samples are lower in ^{18}O than most analyzed schists and gneisses throughout the world; the latter typically have $\delta^{18}O$ values between +10 and +18 (Garlick and Epstein, 1967; Shieh and Taylor, 1969a; Schwarcz, Clayton, and Mayeda, 1970). However, most of these higher –^{18}O rocks are pelitic or semi-pelitic in composition. High-grade metamorphic rocks such as granitic gneisses and granulites (Taylor, 1969; Wilson, Green, and Davidson, 1970; Shieh and Schwarcz, 1974) approach the $^{18}O/^{16}O$ ratios of igneous rocks. The Lewisian represents a polymetamorphic terrane that has undergone an early granulite-facies metamorphism and at least two separate amphibolite-facies metamorphic events, as well as mylonitization and faulting events (Bowes, 1969; Lambert and Holland, 1972; Moorbath and Park, 1971). Thus, very early in its evolution, the Lewisian samples may have attained oxygen isotopic compositions approaching those of most igneous rocks. Inasmuch as many of the samples are essentially tonalitic to dioritic in composition, they also could have started out with igneous $\delta^{18}O$ values.

Within the Tertiary intrusive complex, two xenoliths of Lewisian gneiss from Harker's Gully and one granite sample from the Eastern Red Hills believed to be Lewisian granite (John Esson, written commun., 1975) have also been analyzed. The results are presented in table 3. These rocks have all clearly been affected, to various degrees, by the Tertiary meteoric-hydrothermal activity at Skye. Sample 407, the most "normal" Lewisian sample in terms of petrographic and structural characteristics, has been depleted by about 3 per mil compared with the Lewisian gneisses from Sleat. The $\delta^{18}O$ values of samples 406 and 407 are isotopically similar to the nearby Southern Porphyritic felsite and Marsco epigranite (fig. 3), suggesting that all these rock types have been similarly affected by the meteoric-hydrothermal alteration. More significant is the fact that the near-normal $\Delta^{18}O_{Q-F}$ value of 1.2 for sample 406 suggests that ^{18}O-depletion of this rock occurred at depth at very high temperatures, high enough that the $\delta^{18}O$ values of both the quartz and feldspar were lowered by similar amounts. The $\delta^{18}O$ values in the Lewisian sample 428 are practically identical to those in the nearby Allt Fearna granite (see fig. 4). In fact, if it were not for its coarser grain size and different trace element chemistry (John Esson, written commun., 1975), we would have concluded from the $\delta^{18}O$ data that this sample is a Tertiary granite similar to the rest of the Red Hills granites. The occurrence of such low-^{18}O Lewisian rocks is compatible with the hypothesis that many of the low-^{18}O Tertiary granitic magmas in the Red Hills (see below) might

TABLE 3

Oxygen isotope data on samples of Lewisian rocks from within the central intrusive complex.

Sample	Mineral	$\delta^{18}O$(‰)	Remarks
406	Q	+2.6	Granite xenolith from Harker's Gully. Q and K
	K	+1.4	(~1mm) in a groundmass of Q, K, and F
	WR	+2.6	(0.1mm); K is cloudy to turbid; minor biotite, chlorite, and amphibole.
407	Q	+5.2	Gneissic xenolith from Harker's Gully. Q and F
	WR	+4.2	(partially altered to epidote and sericite), locally granophyric; relict gneissosity defined mainly by epidote, biotite, and chlorite.
428	Q	+4.1	Granite, tectonic slab at northwest margin of
	F	−4.2	Allt Fearna granite. Sericitized F and K (3mm)
	K	−2.9	with dusty Q (1 mm); minor chlorite, biotite,
	WR	−2.4	and epidote.

Q = quartz; K = K-feldspar; F = plagioclase; WR = whole rock.

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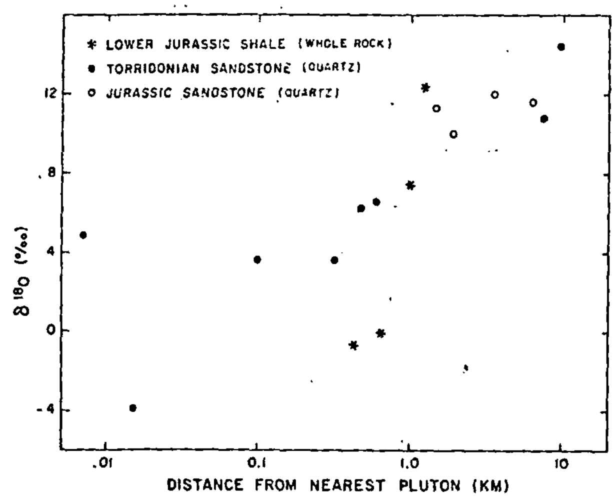

Fig. 6. Semilogarithmic plot of $\delta^{18}O_Q$ of Torridonian and Jurassic sandstones and $\delta^{18}O_R$ of Jurassic shales versus distance from nearest Tertiary pluton.

have formed by partial melting of hydrothermally altered Lewisian basement.

Torridonian and Jurassic sandstones and shales.—The Precambrian Torridonian rocks of Skye have been variously affected by the Tertiary meteoric-hydrothermal activity; the effects seem to be mainly a function of distance from the central intrusive complex (fig. 6). The $\delta^{18}O$ depletions observed in quartz samples extend outward only about 1 km.

The most significant aspect of the isotopic data from the Torridonian rocks is that the meteoric hydrothermal convection systems must have penetrated downward *at least* to the level of the lowermost section of flat-lying sedimentary rocks present in the Skye area. This means that, at a minimum, the convective circulation went down essentially to the unconformity with the basement Lewisian gneiss.

Torridonian sample SK-63 ($\delta^{18}O = -3.9$) is the most ^{18}O-depleted quartz sample yet analyzed from the Scottish Tertiary Province, except for that of the Grigadale granophyre in Ardnamurchan (−6.0; Taylor and Forester, 1971). SK-63 is from the Creag Strollamus area of Skye (King, 1953), a complex region where highly fractured and "granitized" Torridonian is spatially associated with Tertiary volcanic rocks, the Broadford gabbro, and granitic intrusions. Inasmuch as "normal", unaltered Torridonian sandstone has $\delta^{18}O_Q \geqslant +10.8$, the quartz in SK-63 must have been lowered in ^{18}O by about 14 to 15 per mil! The Torridonian here is so intimately invaded and affected by granite that King (1953) regarded the granites as having formed by the *in situ* granitization of Torridonian. The highly sheared and fragmented nature of this sample, and its intimate association with igneous intrusions, apparently aided the oxygen isotopic exchange process.

The Middle Jurassic sandstones of Skye (Morton, 1965) have exceedingly uniform $\delta^{18}O$ values (fig. 6), typical of sedimentary sandstones elsewhere in the world (Savin and Epstein, 1970c). Three sandstone samples from the Strathaird Peninsula have $\delta^{18}O_Q = +11.3$, $+11.6$, and $+12.0$, while another has $\delta^{18}O_R = +13.0$. A sample collected from the contact of the Rudh an Eireannaich sill near Broadford has $\delta^{18}O_Q = +10.0$; its $\delta^{18}O$ value may have been lowered slightly by the hydrothermal alteration that reduced the $\delta^{18}O$ values of the sill to values of 0.1 to 1.4.

Some of the Torridonian and Jurassic quartz samples have apparently been lowered in ^{18}O much more drastically than quartz from the Red Hills granites (see below). This is probably a reflection of (A) the finer grain size of the sandstone quartz with respect to the granitic quartz, (B) the highly fractured and sheared nature of the most ^{18}O-depleted sandstone quartz, (C) the sandstones being more permeable than the Red Hills granites, and (D) the fact that in any convective closed-system meteoric-hydrothermal exchange process, the feldspars will exchange oxygen with the fluid much more readily than the quartz. Thus, in the granite the H_2O will undergo a relatively rapid ^{18}O enrichment as a result of exchange with feldspar, and this high-^{18}O H_2O will then not be able to produce significant ^{18}O depletion of the coexisting granite quartz.

Similar to the relationship shown by the Torridonian, there is an excellent correlation between $\delta^{18}O_R$ of the Jurassic shales and their proximity to the nearest major intrusion (fig. 6). The $\delta^{18}O_R$ values of most shales elsewhere in the world are about +14 to +19 (Silverman, 1951; Taylor and Epstein, 1962b; Savin and Epstein, 1970b). Thus some of these shale samples from Skye probably have been lowered in ^{18}O by more than 14 per mil.

Cambro-Ordovician Durness limestone.—The Durness limestone forms a uniquely important rock unit involved in the Tertiary hydrothermal activity, as discussed below in connection with the BDG. Typical sedimentary carbonate rocks have well-defined $\delta^{18}O$ values of about +18 to +25 and $\delta^{13}C$ values of about −1 to +1 (Keith and Weber, 1964; Degens and Epstein, 1962). The samples of the Durness limestone analyzed in this study deviate strongly from these "normal" values, ranging from −0.6 to +21.4 ($\delta^{18}O$), and −5.1 to −1.0 ($\delta^{13}C$) (fig. 7). Except for the most $\delta^{18}O$-depleted sample, the dolomites have heavier $\delta^{13}C$ and $\delta^{18}O$ values than coexisting calcites in the same sample. This is the expected relationship at isotopic equilibrium, but in this case it is more likely a result of the fact that dolomites were more resistant to isotopic exchange with H_2O than were the calcites. Isotopic disequilibrium beween dolomite and calcite is particularly apparent in skarn sample SK-42 and is analogous to the type of oxygen isotopic disequilibrium observed in almost all coexisting silicate minerals in the Skye intrusive complex.

Note that there is a positive correlation shown in figure 7 between $\delta^{13}C$ and $\delta^{18}O$. The slope of the best-fit line through these Durness car-

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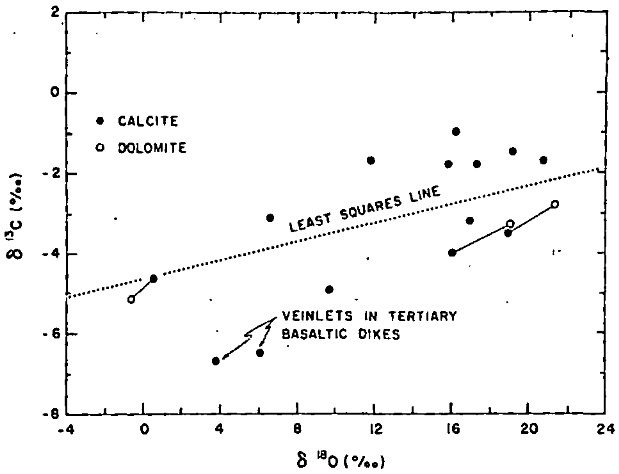


Fig. 7. Plot of $\delta^{13}C$ versus $\delta^{18}O$ for carbonates from the Durness limestone of Skye. A least-squares straight line calculated from the data (slope = 0.12) is also shown. Tielines connect coexisting calcite–dolomite pairs.

bonate data-points is 0.12. If we assume that CO_2 was the dominant oxygen-bearing fluid evolved during decarbonation and skarn formation from these dolomites, then the isotopic changes in the carbonates may have approximately followed a Rayleigh-type distillation with $R = R_o f^{\alpha-1}$ or $\delta - \delta_o \cong 10^3 (\alpha - 1) \ln f$, where f represents the fraction of CO_2 remaining at any stage of the process. This type of equation would apply to both $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios. For example, if the reactions over the whole of the Durness limestone occurred, on the average, at approximately 350°C, the equilibrium values are $\alpha^{13}C_{calcite\text{-}CO_2} = 0.9976$ and $\alpha^{18}O_{calcite\text{-}CO_2} = 0.9900$ (Bottinga, 1968). Thus the evolution of CO_2 on a $\delta^{13}C$-$\delta^{18}O$ diagram will be represented by a line of slope $(\alpha^{13}C-1)/(\alpha^{18}O-1)$ or 0.24. This slope is significantly different than that defined by the isotopic data of the Cambro-Ordovician Durness limestone. It is however similar to the slopes defined by contact metamorphic marbles studied by Deines and Gold, 1969 (slope $\cong$ 0.28) and Shieh and Taylor, 1969b (slope $\cong$ 0.25). Thus the equilibrium Rayleigh-type model affords a qualitative explanation for the distribution of points on $\delta^{13}C$ versus $\delta^{18}O$ plots for these two earlier studies of contact metamorphism, but it cannot quantitatively explain the Durness carbonate data, unless the α values are modified by kinetic factors or other non-equilibrium effects. The above discussion emphasizes the fact that another process must have operated in the evolution of the recrystallized Durness limestone, probably exchange with low-^{18}O hydrothermal fluids at the time of the major meteoric-hydrothermal alteration events on Skye. In fact, some meteoric water *must* have penetrated the limestone unit in order to reach the Beinn an Dubhaich granite (see below).

The effect of isotopic exchange with the ground waters would be to lower the $\delta^{18}O$ values of the carbonates; those skarn samples that have

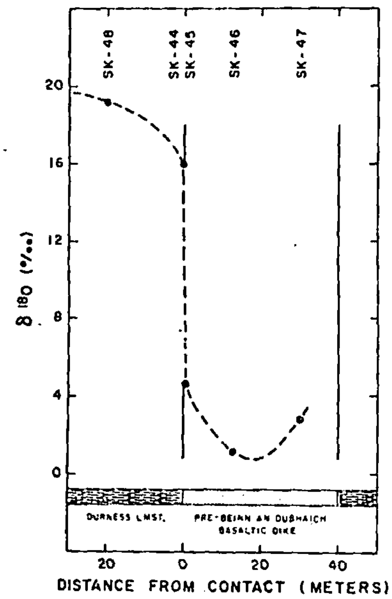
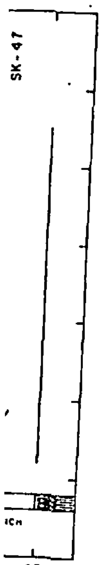


Fig. 8. Plot of $\delta^{18}O$ versus distance for whole-rock samples in the immediate vicinity of a composite, pre-BDG basaltic dike that intrudes the Durness limestone.

been most strongly metamorphosed apparently have also undergone the most ^{18}O exchange with heated meteoric waters. The latter process would have little if any effect on the $\delta^{13}C$ values, inasmuch as the carbon reservoir is essentially the carbonate unit itself. Hence, it appears that two processes acted essentially simultaneously during the recrystallization of the Durness limestone: (1) evolution of CO_2 following a normal Rayleigh-type distillation pattern, and (2) exchange with heated meteoric ground waters. Note that a stable isotope study by Tan and Hudson (1971) on the carbonates of the Great Estuarine Series (Jurassic), Scotland, showed that the majority of the carbonates have normal $\delta^{18}O$ values of +25 to +30. However, those in the vicinity of the central intrusive Tertiary complexes show significant ^{18}O-depletion. For example, the calcites on the shore north of Elgol on Strathaird Peninsula have $\delta^{18}O = +22.5$ to $+12.3$, whereas the more resistant dolomite has $\delta^{18}O = +27.8$ to $+18.5$.

Two calcite veinlets from the Tertiary basaltic dikes of Skye are also plotted in figure 7. Note that their $\delta^{13}C$ values (–6.7; –6.5) are compatible with a deep-seated igneous origin for the carbon (Deines and Gold, 1973; Deines, 1970; Taylor, Frechen, and Degens, 1967), whereas the $\delta^{18}O$ values can be accounted for by crystallization between 150° and 200°C from meteoric H_2O with $\delta^{18}0 \cong -6$ (O'Neil, Clayton, and Mayeda, 1969).

There are some interesting isotopic relationships exhibited at the contacts between the limestones and the intrusive dikes. A 40 m thick composite dike which cuts the Durness limestone, but is truncated by the Beinn an Dubhaich granite, was sampled in detail (fig. 8). The $\delta^{18}O$



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gradient at the contact is approximately 20 per mil/m over a distance of about 0.5 m. The symmetrical distribution of $\delta^{18}O$ values across the dike suggests that this multiple dike occupies a major pre-granite fracture through which there was circulation of meteoric-hydrothermal fluids. Continued fracturing and magma injection led to strong ^{18}O depletion of the main part of the dike ($\delta^{18}O_R \cong +1$), but interaction between the margins of the dike and the high-^{18}O Durness limestone increased the $\delta^{18}O$ values near the contact to about +4 or +5. There is also a possibility, however, that this basaltic dike may have originally been intruded as a low-^{18}O magma, which then simply exchanged at its margins with the limestone.

CUILLIN GABBRO COMPLEX

On the basis of a few analyzed specimens from the Cuillin Hills, Taylor and Forester (1971) suggested that the $\delta^{18}O$ values increase toward the interior of the complex. The present study substantiates that preliminary conclusion, but the new data also make it clear that all the minerals from the *entire* Cuillin layered complex (figs. 2 and 9), as well as the dike rocks which cut it, are abnormally low in ^{18}O.

The variation in ^{18}O across the Cuillin complex is shown diagrammatically in figure 9. Note that the $\delta^{18}O_P$ values are relatively constant but are 2 to 3 per mil lower in ^{18}O than the pyroxenes from "normal" gabbros and basalts. The $\delta^{18}O_F$ values are even lower and are much more variable than the pyroxene values, but they do exhibit some systematic relationships with respect to geographic position within the complex, as follows: (1) The most positive $\delta^{18}O_F$ values define an ovoid central core with $\delta^{18}O >$ zero in the vicinity of the southeast end of Loch Coruisk; this high-^{18}O zone is confined mainly to the upper part of zone I and lower part of zone II of the Eucrite Series. (2) The $\delta^{18}O$ variations in the plagioclase are, however, *not* controlled by the various primary igneous stratigraphic units of the Cuillin layered series, as shown by the fact that as one moves east or west in zone II away from the ovoid central core, the $\delta^{18}O$ values of the plagioclase decrease to −5.6 and −3.0, respectively (see fig. 2). (3) The most ^{18}O-depleted plagioclases are found in close proximity to the outer contacts, either with the earlier plateau basalts on the southwest or with the later granites and the volcanic vents on the northeast. It is thus only a coincidence of geographic position that most of the extremely low $\delta^{18}O$ values are found in the lowest stratigraphic unit, zone I (near the basalts), or the highest stratigraphic unit, the Gabbro Series (near the Western Red Hills granites).

We would *a priori* predict on the basis of the meteoric-hydrothermal model that, for the intrusion of an epizonal pluton into basaltic country rocks, the least affected rocks would be those in the core region of the intrusion; $\delta^{18}O_{H_2O}$ generally increases as the degree of water-rock interaction and isotopic exchange proceeds, so the initial isotopic contrast between the water and rock would diminish both with time and with distance of penetration of the H_2O into the central core of the intrusion (for

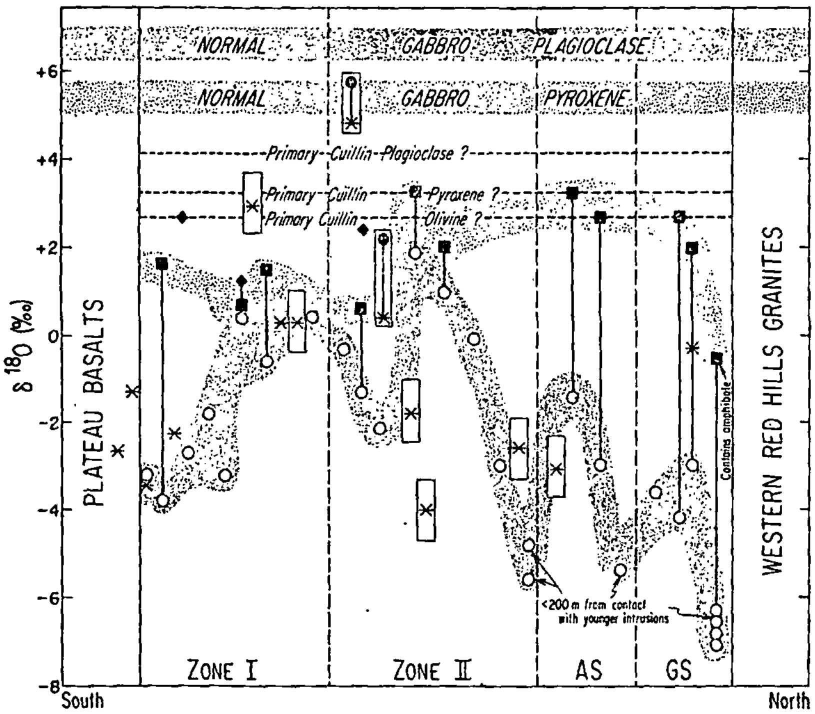
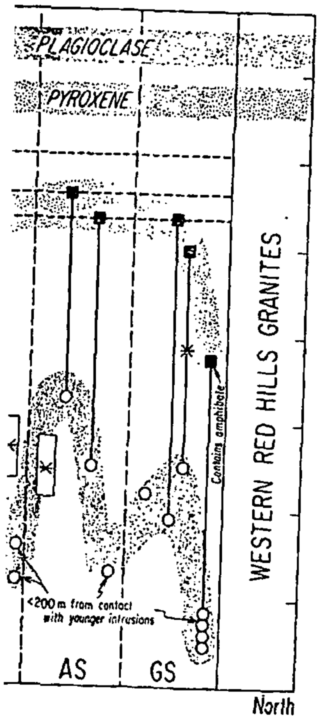


Fig. 9. Generalized graph of $\delta^{18}O$ values of minerals within the Cuillin gabbro, as a function of position in the layered series (open circles = plagioclase, solid circles = quartz, squares = pyroxene, diamonds = olivine, crosses = whole rock). The subdivisions zone I and zone II of the Eucrite Series, the Allivalite Series (AS), and the Gabbro Series (GS) are after Wager and Brown (1967). Values for dike rocks are enclosed in rectangles. The vertical tie lines indicate coexisting minerals. Also shown are the $\delta^{18}O$ values of plagioclases and pyroxenes of typical gabbros throughout the world (horizontal bands) and the $\delta^{18}O$ values of hypothetical primary igneous plagioclase, pyroxene, and olivine that crystallized from the original Cuillin gabbroic magma (dashed lines; see text).

example, see fig. 9, Taylor, 1971). The distribution of ^{18}O contours may originally have been fairly symmetric directly after emplacement and crystallization of the Cuillin complex, but the pattern was probably then modified by later periods of oxygen isotope exchange that accompanied meteoric-hydrothermal convection systems established during and just after intrusion of the younger vent agglomerates and Western Red Hills granites; this produced the low $\delta^{18}O$ values in the northeastern part of the Cuillin complex, giving the final pattern shown in figures 2 and 9. Note that a $\delta^{18}O_F = -4$ contour could be drawn on figure 2 that closely parallels the contacts between the gabbros and the Western Red Hills granites and explosion breccias; all the Cuillin $\delta^{18}O_F$ values lower than −4 are from samples that lie within 200 m of the contacts with these younger intrusions, and the low $\delta^{18}O$ values therefore must be a result of hydrothermal contact metamorphism.



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The fact that the plagioclase $\delta^{18}O$ variations do not correlate directly with the primary igneous structural subdivisions (and cryptic compositional variations of the minerals) indicates that these $\delta^{18}O$ variations were largely imposed after crystallization of the Cuillin magma body. However, it is even more clear from the $\delta^{18}O$ data on coexisting plagioclase and pyroxene that subsolidus exchange of oxygen isotopes was the dominant process. Normal $\Delta^{18}O_{F\text{-}P}$ values from gabbroic rocks are about +1.0 (Taylor, 1968), whereas in the Cuillin gabbros these Δ-values are invariably negative (see fig. 9). Thus *all* the plagioclases must have been lowered in ^{18}O to some extent after they crystallized, but the pyroxenes have been much less affected. Some of the plagioclases have apparently been lowered to a remarkable degree, by 13 or 14 per mil. As in prior studies of this type, it is clear from the data presented in figure 9 that of the several minerals in the gabbros, the plagioclase is by far the most susceptible to oxygen isotope exchange. There is, however, no correlation between grain size and $\delta^{18}O$ for the plagioclase. In fact, several samples exhibiting a wide variation in grain size were collected at a single locality (AS zone, fig. 2); the medium-grained plagioclase turned out to have a slightly more "normal" $\delta^{18}O(-1.4)$ than the plagioclase of the pegmatitic gabbro ($\delta^{18}O = -3.0$). A similar lack of any relationship between grain size and $\delta^{18}O$ also holds for the coexisting pyroxene. A plausible explanation for this is that the pegmatitic gabbro itself may be a recrystallized rock formed at subsolidus temperatures by interaction with the high-temperature, meteoric-hydrothermal solutions.

Four different plagioclase separates were analyzed from SK-219, the most ^{18}O-depleted rock from the Cuillin complex (GS zone, fig. 2). In order of increasing magnetic susceptibility, the plagioclase $\delta^{18}O$ values are −6.3, −6.7, −6.9, and −7.1, respectively. The ^{18}O variation is outside analytical error. Each magnetic separate gave identical oxygen yields consistent with the mineral separate being pure calcic plagioclase, although the more magnetic samples do contain more of the dust-like, opaque inclusions (presumably magnetite). It is interesting that the lowest $-^{18}O$ separate contains the greatest abundance of opaque inclusions, suggesting that the dusty, cloudy appearance of the plagioclase may itself have been produced by subsolidus hydrothermal exchange. The heterogeneous oxygen isotope distribution in the SK-219 plagioclase is yet another indication of isotopic disequilibrium and subsolidus exchange. These same conclusions apply to SK-226, where two different magnetic separates of plagioclase have $\delta^{18}O = -4.8$ and −5.6.

The striking uniformity of the pyroxene $\delta^{18}O$ values, particularly as compared to the plagioclase $\delta^{18}O$ data, suggests that the parent Cuillin gabbroic melt may itself have been an ^{18}O-depleted magma. If the original Cullin magma had a "normal" $\delta^{18}O$ of about +6.0, we would expect the primary igneous clinopyroxene to have had $\delta^{18}O \cong +5.5$ (fig. 9). Inasmuch as most of the Cuillin clinopyroxenes now have $\delta^{18}O \cong +2$ to +3, they would all have had to undergo approximately equal depletion in ^{18}O. However, why should the extent of ^{18}O depletion in the pyroxene suddenly halt everywhere at about the same value, while the coexisting plagioclase continued to exchange to widely varying degrees? It is much more likely that all the primary igneous pyroxenes *originally* had $\delta^{18}O \cong +3$, as shown on figure 9, and that subsequently there were variable, local ^{18}O-depletions of up to 2 per mil during subsolidus exchange.

The relatively uniform $\delta^{18}O$ values of 3 olivines (+2.7, +2.4, +1.3) support the above hypothesis, as an olivine with $\delta^{18}O \cong +2.5$ would be in equilibrium at magmatic temperatures with a clinopyroxene with $\delta^{18}O \cong +3.0$ (Anderson, Clayton, and Mayeda, 1971). It thus appears that the parent Cuillin gabbroic magma may have been a low-^{18}O silicate melt with $\delta^{18}O \cong +3.5$ instead of the "normal" value of +6.0. The original plagioclase, pyroxene, and olivine that crystallized from such a magma could have had the $\delta^{18}O$ values shown by the horizontal dotted lines on figure 9. This hypothesis is made more plausible in the light of the evidence for extensive extrusion of low-^{18}O basaltic magmas on Iceland, some with $\delta^{18}O$ values as low as +2 to +3 (Muehlenbachs, Anderson, and Sigvaldason, 1974).

It is difficult to estimate the temperatures at which the subsolidus exchange in the Cuillin gabbros occurred, but it is probable that only near the younger Red Hills intrusions were the final exchange temperatures typically as low as 300° to 500°C. This is because the plagioclase and pyroxenes are everywhere else so remarkably fresh and unaltered. Even more striking is the fact that much of the olivine is so well preserved, as this indicates that essentially *all* of the hydrothermal ^{18}O exchange that affected the fresh olivine gabbros and unserpentinized peridotites must have taken place at temperatures that were above the stability field of serpentine (that is, above approximately 500°C, Tuttle and Bowen, 1949). *After* the high-temperature exchange occurred, the olivine-bearing rocks must then all have become largely isolated from any low-temperature meteoric-hydrothermal fluids. This is plausible because the fresh olivines are largely confined to the central part of the gabbro complex, and it is significant because it demonstrates that olivine and pyroxene are fairly resistant to hydrothermal ^{18}O exchange even at temperatures above 500°C.

The Cuillin gabbros are riddled by fractures and veins, readily visible both on the outcrops (pl. 1) and in thin sections, so even though the rocks are *mineralogically* little altered it is easy to visualize the pathways of the meteoric-hydrothermal fluids. It is important to emphasize the concept that even though there is very little development of new minerals such as actinolite, chlorite, and epidote in these rocks, the rocks have *all* been intensely hydrothermally altered. However, because much of this alteration occurred at high temperatures soon after solidification, the only direct evidence of the extensive hydrothermal activity is provided by the $^{18}O/^{16}O$ data.

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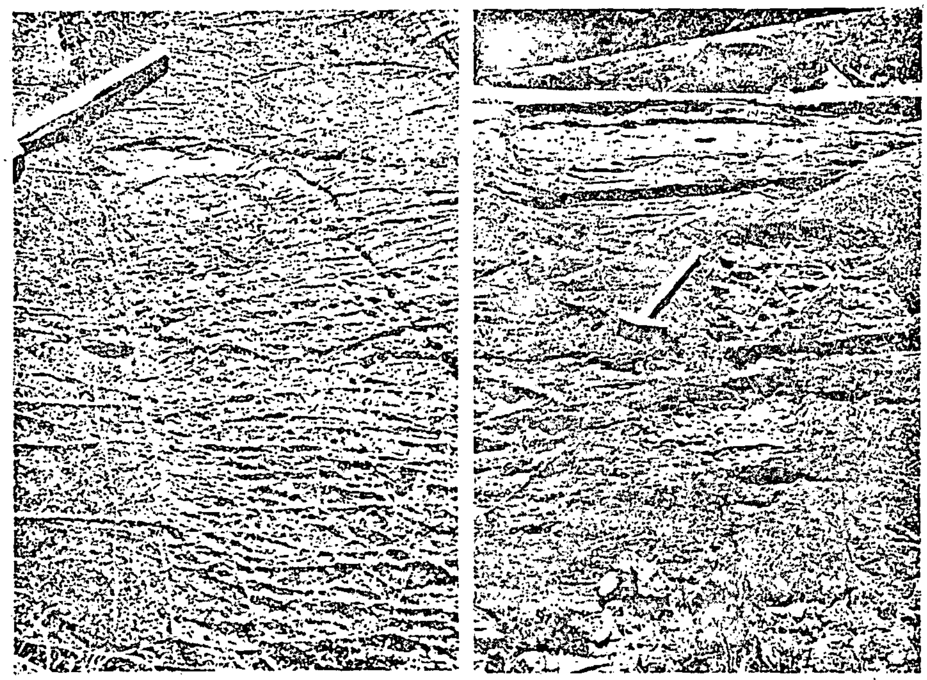
PLATE 1



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A. Outcrop of Cuillin gabbro, cut by a myriad of veins that represent pathways for meteoric-hydrothermal fluids. Zone II of the eucrite series, southwest side of Loch Coruisk.

B. Outcrop of Cuillin gabbro, containing less resistant periodotite blocks cut by numerous veins. Zone II of the eucrite series, on the southwest side of Loch Coruisk.

OTHER GABBROS

In contrast to the Cuillin gabbros, the gabbros from the Creag Strollamus area (King, 1953) exhibit appreciable mineralogical evidence for hydrothermal alteration. Thus they apparently suffered meteoric-hydrothermal isotopic exchange down to much lower temperatures than did the Cuillin gabbros. For example, the Broadford gabbro has $\delta^{18}O = -2.7$ to -4.2 and contains abundant uralite ($\delta^{18}O = -1.9$, SK-51), whereas the Cuillin gabbro underwent partial amphibolitization of the pyroxenes mainly in those rocks adjacent to the Western Red Hills granites. The reason for this difference probably lies in the fact that the Broadford gabbro is close to, and has been affected by, the many granitic intrusions of the Eastern Red Hills, whereas the Cuillin complex *in general* is relatively further removed from the subsequent intrusive plutonic centers.

The minor gabbroic bodies that intrude Mesozoic sedimentary rocks well outside the central intrusive complex have been little affected by the heated meteoric ground waters (fig. 4). This is a result of their peripheral locations and their relatively small volume, as well as to the impermeable nature of the enclosing Mesozoic shales. It is not surprising, therefore, to have $\delta^{18}O_R = +7.9$ (SK-74) for a gabbroic dike cutting the shales, with the contact gabbro having $\delta^{18}O_R = +9.1$ (SK-25). Here is an apparent example of ^{18}O-*enrichment* due to contamination or isotopic exchange with the ^{18}O-rich country rock shales; similar effects in larger intrusions have been described by Turi and Taylor (1971a,b) and Shieh and Taylor (1969a). Note also the near-normal $\delta^{18}O$ values of the dikes and composite sills near Rudha Suishnish ($\delta^{18}O = +6.9, +6.4, +5.8$), Elgol ($\delta^{18}O = +4.8$), and those farther north (+5.2; +4.3).

COIRE UAIGNEICH GRANOPHYRE (CUG)

The Coire Uaigneich granophyre is an elongate, sinuous intrusion lying to the east of the Cuillin complex (fig. 2). Its age is pre-Red Hills granites but post-Cuillin gabbros. Wager, Weedon, and Vincent (1953) and Brown (1963) provided evidence that this granophyre, which contains inverted tridymite, may be a melting product of the Torridonian sandstone. Three granophyre samples have $\delta^{18}O_R = -2.5, -1.3$, and $+0.5$, and the Torridonian sandstones collected well away from the central intrusive complex have an average $\delta^{18}O \cong +11$. Thus, if the CUG does represent melted Torridonian, there must have been a major change in $\delta^{18}O$.

Modifying the basic model of Brown (1963), and assuming that the Torridonian in contact with the Cuillin intrusion was partially melted in the presence of meteoric ground waters at about 300 bars P_{H_2O} and 970°C, we can only account for 10 percent of the observed 12 per mil ^{18}O depletion by direct influx of low-^{18}O H_2O into the melt. The remaining 11 per mil of ^{18}O depletion must have been produced either by later hydrothermal alteration, or else the granophyre melt was formed by partial fusion of Torridonian sandstones that had already been hydrothermally altered and depleted in ^{18}O by at least 10 per mil *prior* to melting. Note that some Torridonian samples within the central intrusive complex have been lowered even more than this, for example, in the Creag Strollamus area and north of Meall Buidhe (see figs. 4 and 6). It is thus possible that the Coire Uaigneich granophyre was intruded as an extreme low-^{18}O magma, because it is doubtful that such consistently low $\delta^{18}O$ values would have been produced by the hydrothermal systems associated with the Western Red Hills granites, whose nearest outcrops are more than 2 km distant. Here is a possible example where meteoric waters may have been partially responsible for *generating* a melt, because dry melting of a rock with such a high SiO_2 content requires an unrealistically high temperature of about 1200°C (Brown, 1963).

It is, however, also possible that the CUG was intruded at the same time that the hydrothermal convective circulation system associated with the Cuillin gabbro complex was operating. This timing is compatible with the geological age relationships, and thus the low $\delta^{18}O$ values of the CUG conceivably could in large part be a result of subsolidus hydrothermal alteration. This raises another possibility, namely that the high SiO_2 content of the CUG might be due to late-stage silicification asso-

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RED HILLS GRANITES

The $\delta^{18}O$ values of all quartz and feldspar samples from the Red Hills granites are plotted in figure 10 as a function of sequence of intrusion. The relative ages of intrusion of these granites have been established solely by geologic field mapping (see Stewart, 1965) and are definitively determined only for the Western Red Hills granites. The major geologic discontinuties are, however, well established and include: (1) the break between the Western and Eastern Red Hills; (2) the break within the Western Red Hills after the intrusion of the Loch Ainort epigranite, but before the Southern Porphyritic epigranite; and (3) the break in the Eastern Red Hills before and after emplacement of the Kilchrist volcanic vent. In general, there was a major shift in the focus of ring dike intrusion at each of these discontinuities.

The isotopic data in figure 10 are grouped according to these geologic discontinuities in the sequence of granitic intrusion, and although there is appreciable scatter in the isotope data, the age discontinuities also seem to correlate with breaks in the $\delta^{18}O$ data. In particular the most abrupt change in the $\delta^{18}O$ trend of quartz occurs at the major geological discontinuity, namely between the Marsco epigranite of the Western Red Hills and the Glas Beinn Mhor epigranite of the Eastern Red Hills. The average $\delta^{18}O_Q$ of each of the 4 groups on figure 10 is relatively uniform, but the average $\delta^{18}O_K$ increases in the later intrusions, up to the stage of intrusion of the Beinn an Dubhaich granite. All the quartz and feldspar samples are lower in $\delta^{18}O$ than those from "normal" granites.

Euhedral minerals in the miarolitic cavities of the Loch Ainort epigranite (Western Red Hills) and Beinn na Caillich granophyre (Eastern Red Hills) have large $\Delta^{18}O_{Q\text{-}K}$ values that are basically similar to the host-rock minerals of these granites. This indicates that the same general types of subsolidus oxygen isotope exchange processes also affected the minerals of the miarolitic cavities. However, in a given pluton, these euhedral quartz and feldspar crystals do tend to have lower $\delta^{18}O$ values than the host rock minerals (fig. 10), compatible with their direct crystallization from a low-^{18}O aqueous gas phase in a somewhat higher meteoric water/rock environment. For example, three different samples of miarolitic quartz from a single hand specimen of the Loch Ainort epigranite have $\delta^{18}O$ = +1.7, +2.5, and +3.0, all lower in ^{18}O than the host-rock quartz ($\delta^{18}O$ = +4.1). Therefore, the miarolitic cavities were probably produced by late stage influx of meteoric-hydrothermal fluids into the crystallizing granite plutons.

WESTERN RED HILLS

Feldspar $\delta^{18}O$ values.—Let us apply the meteoric-hydrothermal model in an attempt to explain the first-order features shown by the isotopic data from the Western Red Hills, namely the fact that much larger ^{18}O depletions in feldspar are seen in the earlier granites than in the later intrusions. Each successive arcuate pluton was commonly intruded along a ring fracture interior to an earlier pluton, and upon intrusion of each pluton, a new hydrothermal convective system ought to have been established or an older, preexisting system modified. Other things being equal, we would then predict that the older intrusives would experience a greater number of overlapping hydrothermal alteration events (and hence more ^{18}O depletion) than the younger intrusions. Another factor that may be important is that the older intrusions on the outside of the

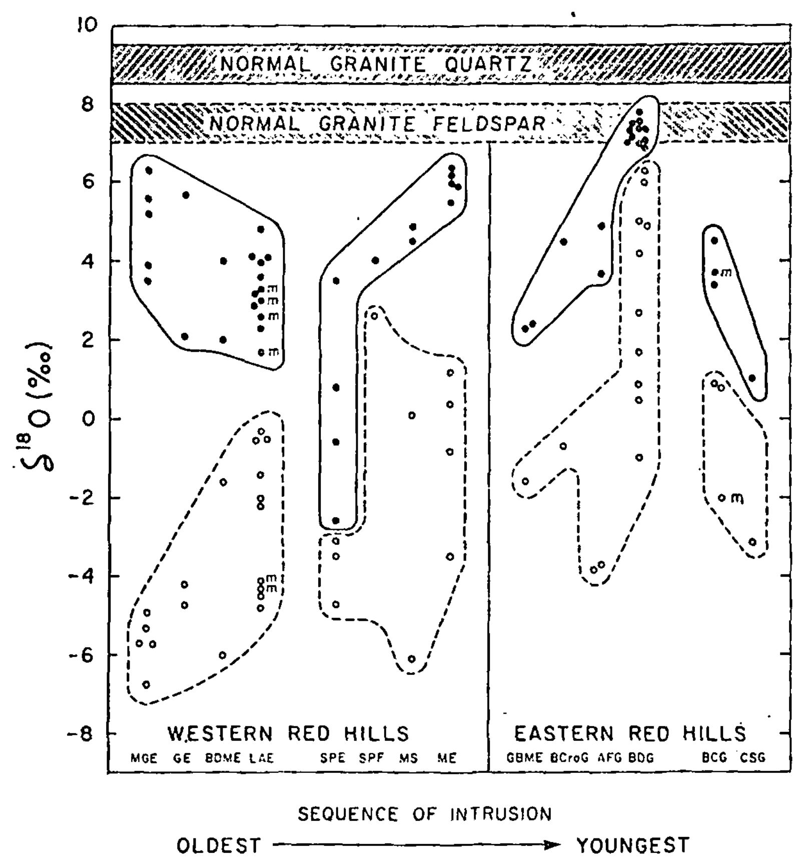

Fig. 10. Plot of $\delta^{18}O_Q$ (solid circles) and $\delta^{18}O_K$ (open circles) versus age of intrusion for the granites of the Western and Eastern Red Hills. The break in the Western Red Hills is between the Early Epigranites and the Later Intrusions. Sequence is from Wager and others (1965) and Stewart (1965); also see Forester (ms). The $\delta^{18}O$ values of quartz and feldspar from most granitic rocks throughout the world are typically at least as high as +9.0 and +7.5, respectively, as indicated by the horizontal bands. The symbol *m* indicates the mineral is from a miarolitic cavity. The other analyses should be reasonably characteristic of each pluton, except in the case of the BDG, where all the $\delta^{18}O_K$ values lower than +4 are special samples collected near fractures or from very fine-grained rocks (see fig. 13).

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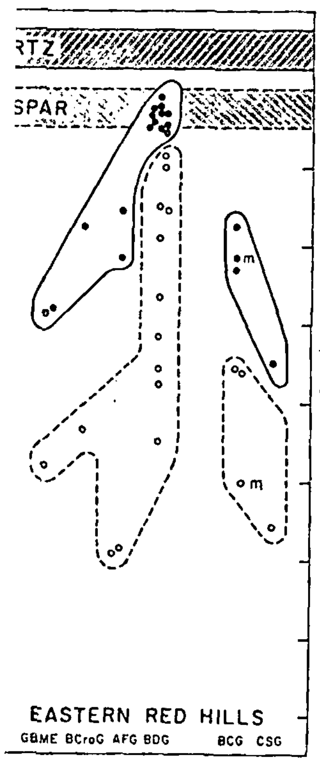

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complex are directly adjacent to the volcanic country rocks, which are very highly jointed and thus probably more permeable to ground water movement than the plutonic intrusions themselves. Also, as time goes on, the meteoric-hydrothermal systems tend to be self-sealing because the older fractures (for example, in the volcanic country rocks) will be filled with vein minerals deposited from the circulating solutions. All these effects are cumulative, and all indicate that the older, outer-most ring intrusions should show the greatest ^{18}O depletions.

Some of the variables that would affect this model are the following: (A) The closer a country rock sample is to the heat source, the higher the temperature of the exchange reaction, and thus the more closely will the sample approach the $\delta^{18}O$ value of the H_2O. This will lead to greater ^{18}O depletions. Added to this is the fact that the higher temperatures promote more rapid and more extensive isotopic exchange, and thus quartz might also be affected as well as feldspar. (B) The larger the volume of the intrusion (heat source), the greater will be the $\delta^{18}O$ change in a sample at a given distance away from the contact, other things being equal. This is because the hydrothermal system associated with the larger plutons will be larger and will persist for a longer time. (C) The susceptibility to oxygen isotope exchange will be dependent on mineralogy and grain size. Quartz-rich rocks and coarser-grained rocks in general ought to be less affected.

In order to make a semi-quantitative test of the above model, we have used the $\delta^{18}O_K$ values (actually 25 samples are alkali feldspar, and three are plagioclase) of the Western Red Hills granites. Feldspar is the mineral most susceptible to oxygen isotope exchange and would best monitor the exchange process. Most of these rocks are of essentially identical mineralogy, as they are all granitic in composition, and quartz and feldspar constitute about 90 percent of each rock. Also, grain size does not vary substantially, and in any event as will be shown below, throughout the igneous rocks of southern Skye, there is a general lack of correlation between $\delta^{18}O_K$ and grain size (except where water/rock ratios are low, as in the case of the Beinn an Dubhaich granite of the Eastern Red Hills).

A function that should provide a semi-quantitative measure of the oxygen isotope-distance relationships discussed above is designated $\sum_j \theta_j$. The term θ_j is defined as being inversely proportional to D, the distance (in km) from a given sample locality to the contact of the intrusive body that has produced the particular (jth) meteoric-hydrothermal system, and also it is defined as being directly proportional to the volume of the intrusion. As the Red Hills intrusions apparently have near-vertical contacts, their respective outcrop areas will accurately reflect their relative volumes. The area function is taken to be the fraction of the invading pluton's area with respect to the area of the whole granitic intrusive complex *at the time of intrusion.* Thus the area fraction is a varying function of time, equal to

$$\frac{a_j}{\sum_{i \leq j} a_i}$$

where a_j is the area of the particular (jth) intrusion producing the meteoric-hydrothermal system, and $\sum_{i \leq j} a_i$ denotes the cumulative area of all intrusions up to the time that the jth intrusion is emplaced. Thus, we define

$$\theta_j = \frac{1}{D_j} \frac{a_j}{\sum_{i \leq j} a_i} \text{ (in km}^{-1}\text{)}$$

For every alkali feldspar analyzed from a given pluton, a θ_j value can be calculated for each subsequent intrusion by measuring the shortest distance D (in km) from the sample to the intrusive contact. We can then sum all of these contributions from each intrusion and obtain $\sum_j \theta_j$ for each sample locality.

If the simplified model discussed above is valid, the samples having the largest values of $\sum_j \theta_j$ should have undergone the greatest depletion in ^{18}O. The isotopic exchange function $\sum_j \theta_j$ is plotted against feldspar $\delta^{18}O$ in figure 11. Except for one point, there is a fairly good correlation between $\delta^{18}O_K$ and $\sum_j \theta_j$ indicating that to a first approximation, the model is a reasonable one.

The only point falling well off the trend in figure 11 is the single sample of Southern Porphyritic felsite (IGC-13). This probably has an anomalously high $\sum_j \theta_j$ value for a $\delta^{18}O_K = +2.6$, because it is less than 80 m from the Marscoite epigranite and Marscoite bodies, and the sample has only experienced the edge effects of these very thin, sinuous intrusions, in spite of the fact that the full volumes of these intrusions are applied to the generation of the $\sum_j \theta_j$ function. Note also that among the samples that have unusually low $\delta^{18}O$ values for a given $\sum_j \theta_j$ value are all three samples of the Southern Porphyritic epigranite, a unit that was probably intruded as a low-^{18}O magma (see below).

Quartz $\delta^{18}O$ values.—Inasmuch as quartz is the most resistant rock-forming mineral to oxygen isotope exchange, its $\delta^{18}O$ value should best reflect the $^{18}O/^{16}O$ ratio of the original magma from which it crystallized. If each intrusion had a homogeneous $^{18}O/^{16}O$ ratio when emplaced as a liquid, then the most positive $\delta^{18}O_Q$ value should be closest to the isotopic composition of the primary igneous quartz prior to meteoric-hydrothermal alteration. The pattern that emerges from the Western Red Hills data in he area fraction is a varying

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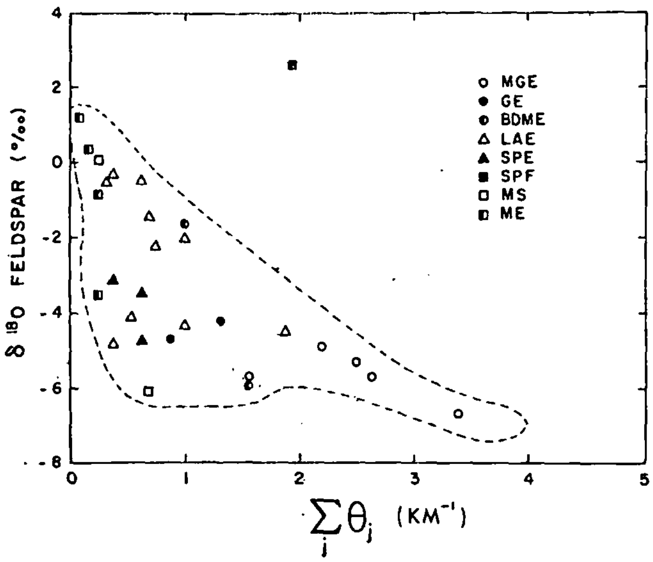


Fig. 11. Plot of $\delta^{18}O_F$ versus $\sum_j \theta_j$ for the granites of the Western Red Hills. For discussion of the meaning of $\sum_j \theta_j$, see text.

figure 10 is that $\delta^{18}O_Q$ *decreases* with time during emplacement of the Early Epigranites but appears to *increase* with decreasing age in the Later Intrusions. These trends might be attributed to chance except that the trends in *both* the Early Epigranites and the Later Intrusions are monotonic functions of time, and the break in sign of the slope of the trend occurs, in time, between the Early Epigranites and the Later Intrusions, which is also a geological and petrological discontinuity. In addition, the fact that there is no correlation between grain size and $\delta^{18}O_Q$ in the Western Red Hills intrusions suggests that the major $\delta^{18}O$ lowering of the quartz might be a primary igneous feature.

As described above in discussing the hydrothermal isotope exchange model, other things being equal, we would expect the older intrusions to be more depleted in ^{18}O than the younger intrusions. In fact, if the $\delta^{18}O$ values of the granite quartz are at all affected by subsolidus exchange, we might *a priori* expect a plot of $\delta^{18}O_Q$ versus age to have a positive slope on this diagram, as is actually shown by the alkali feldspars. Thus, the only plausible explanation why the quartz of the Early Epigranites exhibits a *negative* slope, while the feldspars in the same rocks show the expected positive slope, is that these intrusions were emplaced as low-^{18}O magmas, with the $\delta^{18}O$ of the magmas decreasing progressively with time. A general $\delta^{18}O$-lowering of the magmas with time might perhaps be expected, if meteoric water continuously exchanged with a shallow magmatic reservoir; the youngest magmas tapped off this reservoir would be the most affected because they would have been ex-

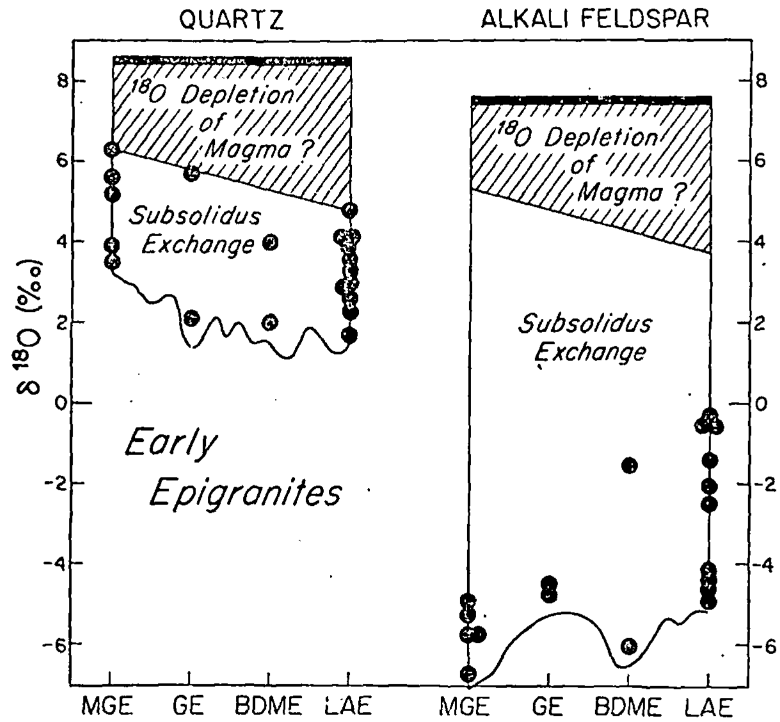
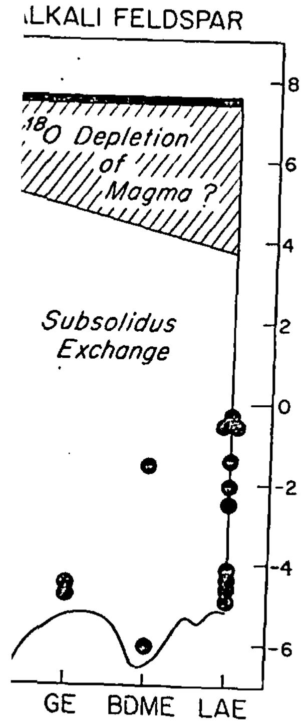


Fig. 12. A model for the Early Epigranites of the Western Red Hills, Skye, comparing the degree of ^{18}O depletion attributed to subsolidus exchange with that due to ^{18}O depletion of the magma (see text). The field labelled ^{18}O depletion of magma is limited by the maximum measured $\delta^{18}O_Q$, assuming the initial $\delta^{18}O_Q = +8.5$ and $\delta^{18}O_K = +7.5$. The measured $\delta^{18}O_Q$ and $\delta^{18}O_K$ values are shown by the dots.

posed to exchange for the longest time. For example, this is the type of trend of $\delta^{18}O$ versus age shown by some rhyolitic ash flow tuff magmas studied by Friedman and others (1974). Another possibility is that if the melts were formed by partial melting of preexisting rocks, as suggested by Pb isotope data (see Moorbath and Welke, 1969; Taylor and Forester, 1971), the younger magmas might be derived from rocks that had undergone progressively greater ^{18}O depletion as the meteoric-hydrothermal activity built up to its maximum.

$^{18}O/^{16}O$ variations as a function of time.—Restricting discussion for the moment to the Early Epigranites, we can develop a self-consistent model to explain the $^{18}O/^{16}O$ systematics of both quartz and alkali feldspar in these granophyric rocks. The model assumes that the *maximum* $^{18}O_Q$ value measured for each pluton represents the value of the primary igneous quartz that crystallized from that particular intrusion (see fig. 10). This model is illustrated diagramatically in figure 12. The $\delta^{18}O$ values of the original granitic magmas appear to have changed from about +5.5 in the early Maol na Gainmhich epigranite to about +4.0 in the later Loch Ainort epigranite. In this model, post-crystallization



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^{18}O depletion of quartz could locally amount to as much as 3 per mil in the Early Epigranites, but the alkali feldspar has later been depleted in ^{18}O during subsolidus exchange by *at least* 6 to 12 per mil irrespective of the model chosen. The two processes (post-crystallization oxygen isotopic exchange and original ^{18}O depletion of the silicate melt) typically appear to contribute approximately equally to the final, measured $\delta^{18}O$ values of the quartz, whereas for alkali feldspar the dominant process is clearly subsolidus exchange. In terms of the whole-rock $\delta^{18}O$ values, typically at least 80 percent of the ^{18}O depletion is due to oxygen isotopic exchange at subsolidus temperatures.

A similar analysis can be done for the Later Intrusions. The simple model discussed above would imply that these magmas increased in $\delta^{18}O$ with time from a value of +3.0 (Southern Porphyritic epigranite) to a $\delta^{18}O$ of +5.5 (Marsco epigranite). Again, regardless of the model, the $\delta^{18}O$ of the feldspars *must* be mainly due to subsolidus ^{18}O depletion, particularly in the case of the Marscoite suite and the Marsco epigranite. However, at least with respect to the Southern Porphyritic epigranite, the concept of initial $^{18}O/^{16}O$ homogeneity of the magma is probably not valid, as discussed below.

Southern Porphyritic epigranite (SPE).—Figure 10 shows that the variation of $\delta^{18}O_Q$ in the SPE (+3.5 to −2.6) is much greater than that displayed by any other intrusion in the *entire* Red Hills area. In addition, the SPE has the lowest $\delta^{18}O_Q$ values yet analyzed from any granophyric rocks of Skye. This is even more remarkable considering that the quartz crystals in this rock are typically euhedral, have β-quartz morphology, and are among the coarsest in grain size of any quartz from the Red Hills intrusions.

The most obvious explanation of the oxygen isotope data is that the SPE was originally intruded as an extremely inhomogeneous, markedly ^{18}O-depleted magma. To test this hypothesis, the following experiments were made. A hand-picked separate of individual euhedral quartz phenocrysts was prepared from the most ^{18}O-rich SPE sample (SK-182; $\delta^{18}O_Q$ = +3.5). This sample (not crushed or ground in any way) was subjected to HF stripping until 82 percent of the original 103 mg sample had been dissolved. The residual quartz had a $\delta^{18}O$ = +5.2, indicating isotopic zoning in the quartz; the outer portions of the quartz that were dissolved away must have had an average $\delta^{18}O$ of about +3.1. This could be explained by partial exchange between the quartz phenocrysts and the meteoric-hydrothermal fluids.

An identical experiment was tried on the most ^{18}O-depleted quartz from the SPE, SK-181. In this case however, after 102 mg of single-crystal quartz phenocrysts ($\delta^{18}O$ = −2.6) were treated with a 48 percent HF solution at room temperature for six hrs, the residual quartz (20 percent of the sample) was analyzed and found to be indistinguishable from the original sample ($\delta^{18}O$ = −2.7). This experiment indicates that these low-^{18}O quartz crystals are isotopically much more homogeneous than those from sample SK-182. However, it should be noted that the residual quartz from the HF stripping experiment did not simply represent the inner cores of the original quartz crystals. Instead, these grains after reaction exhibited a marked dendritic appearance, as a result of the presence of tiny fractures along which the HF caused preferential dissolution of SiO_2. Nevertheless, if these same fractures were present at the time of hydrothermal alteration, the greatest amount of ^{18}O exchange should also have taken place along such cracks. No such effect was found, suggesting that the primary igneous quartz in SK-181 was originally very low in ^{18}O and was relatively inert during the meteoric-hydrothermal alteration (note that if the primary $\delta^{18}O$ value was −2.6, there would have been very little tendency for it to change during the alteration, as it would already be approximately in isotopic equilibrium with the hydrothermal fluids).

In order to examine further the apparent lack of ^{18}O zoning in this quartz sample, a 104 mg sample of single-crystal quartz phenocrysts from SK-181 was subjected to a F_2 stripping experiment, similar to the fluorination stripping experiments described by Epstein and Taylor (1971) on the lunar fines and breccias. The results are given in table 4. For each of the 12 fractions, the sample was reacted with an excess of F_2 at successively higher temperatures for about 30 min, except for the last fraction which was reacted overnight. Because of the low temperatures used (<210°), the first three fluorination fractions yielded almost no oxygen (less than 1μ mol). These initial cuts are therefore not given in table 4, as the isotopic analyses of such small samples ($\delta^{18}O$ = +1.9, −3.4, and −4.8) are very uncertain.

The most striking characteristic displayed in table 4 is the oxygen isotopic uniformity of nearly every fraction analyzed during the F_2 stripping experiment. As expected, the weighted average $\delta^{18}O$ value for the quartz is −2.6. This fluorine stripping experiment demonstrates that the quartz crystals in SK-181 are isotopically homogeneous throughout, whether we are talking about the rims, the cores, or along fractures. These

TABLE 4

$\delta^{18}O$ data obtained by successive fluorination stripping experiment on quartz phenocrysts from Southern Porphyritic epigranite sample SK-181 (see text).

Sample	μmoles O_2	Cumulative μmoles O_2	Cumulative % O_2 extracted	$\delta^{18}O$ per mil
A. 30 min/270°C	~5	~8	0.5	−2.3
B. 30 min/380°C	36	44	2.6	−4.5
C. 30 min/420°C	84	128	7.6	−2.6
D. 30 min/450°C	308	436	25.8	−2.6
E. 30 min/450°C	440	876	51.8	−2.6
F. 30 min/480°C	615	1491	88.2	−2.4
G. 15 min/440°C	50	1541	91.1	−1.7
H. 30 min/440°C	65	1606	95.0	−2.4
I. 16 hrs/560°C	85	1691	100.0	−2.7

oted that the residual quartz simply represent the inner , these grains after reaction as a result of the presence l preferential dissolution of were present at the time of of ^{18}O exchange should also effect was found, suggesting is originally very low in ^{18}O ric-hydrothermal alteration 2.6, there would have been the alteration, as it would ium with the hydrothermal

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Cumulative % O_2 extracted	$\delta^{18}O$ per mil
0.5	−2.3
2.6	−4.5
7.6	−2.6
25.8	−2.6
51.8	−2.6
88.2	−2.4
91.1	−1.7
95.0	−2.4
100.0	−2.7

data are virtually impossible to reconcile with any hypothesis that the Southern Porphyritic epigranite quartz originally crystallized with a "normal" $\delta^{18}O$ value of about +7.0 to +10.0 and subsequently underwent massive oxygen isotope exchange during hydrothermal alteration, completely homogenizing the $^{18}O/^{16}O$ of the quartz and yet perfectly preserving the euhedral hexagonal bipyramids that are indicative of β-quartz crystals. Therefore, the oxygen isotopic homogeneity of the quartz in SK-181 *must* be a primary characteristic imposed on the quartz at the time of its crystallization from an extremely low-^{18}O melt. The above interpretations were reinforced as a result of some later experiments of the same type by Magaritz and Taylor (1976), who demonstrated that high-temperature, meteoric-hydrothermal alteration of granitic rocks from the Coast Range batholith of British Columbia characteristically produced strong isotopic zoning in quartz. The argument is also solidified by noting that SK-181 has essentially a "normal" $\Delta^{18}O_{Q\text{-}K}$ = 0.8, compatible with near-equilibrium crystallization at magmatic temperatures. Although this could be a coincidence, it should be noted that this is the *only* low-^{18}O epigranite from Skye that has a near-normal $\Delta^{18}O_{Q\text{-}K}$ value.

If the SPE was generated as an extreme low-^{18}O magma, why then is there such a large variation in $\delta^{18}O_Q$ at different localities in this rock type? The answer may be related to the manner in which the SPE melt was generated. Like the Coire Uaigneich granophyre, the SPE may have been formed by partial melting of Torridonian arkose (Thompson, 1969). The source rock itself would likely have suffered prior meteoric-hydrothermal alteration and would thus have been isotopically non-homogeneous. Any melting process would then probably give rise to a melt (or melts) that was also inhomogeneous in terms of $\delta^{18}O$. Note that the hydrothermally altered Torridonian sandstones on Skye do in fact show a wide range in $\delta^{18}O$ (fig. 6), with some values as low as −4. Moreover, the SPE and SPF are the most SiO_2-rich and the most MgO- and FeO-poor of all the felsic rocks from the Isle of Skye, including the Coire Uaigneich granophyre. The SPE therefore must have been an extremely viscous magma, too viscous in fact to homogenize itself by convection within the silicate liquid. The SPE is also one of the smaller intrusive bodies of the Red Hills Complex, so it would be easier to develop a silicate melt with such a low $\delta^{18}O$ value. These arguments apply equally well to the Southern Porphyritic felsite and to the Coire Uaigneich granophyre, both of which also may have been intruded as inhomogeneous, low-^{18}O magmas. In addition, because of the somewhat anomalous position of one of the Marscoite suite samples shown on figure 11, it is possible that some of those hybrid intrusions were also low-^{18}O melts.

EASTERN RED HILLS

The early intrusions from the Eastern Red Hills show a $\delta^{18}O$ pattern similar to the Later Intrusions of the Western Red Hills. In general, the maximum $\delta^{18}O$ values from each intrusion increase with time from the

Glas Beinn Mhor epigranite to the Beinn an Dubhaich granite but then decrease with time to the Creag Strollamus granite (fig. 10). However, because the relative age relationships between the various granitic and granophyric bodies are not as well known as for the Western Red Hills (Stewart, 1965), conclusions about these rocks are less firm. The Beinn an Dubhaich granite has unique isotopic characteristics and will be discussed separately in some detail; note that the wide $\delta^{18}O$ range shown for the alkali feldspars of this granite on figure 10 is somewhat misleading, as almost all the feldspars in this intrusion have relatively uniform $\delta^{18}O \cong +4.2$ to $+6.3$. The lower $\delta^{18}O$ values all represent very fine-grained feldspars or special samples collected next to fractures and dikes.

The isotopic discontinuity between the Beinn an Dubhaich granite and the latest granite intrusions on Skye coincides with the emplacement of the agglomerates of the large Kilchrist vent and associated intrusive ignimbrite (Stewart, 1965; Ray, 1960, 1972). It is interesting that the same type of decreasing $\delta^{18}O_Q$ trend is seen here as was evident in the Early Epigranites of the Western Red Hills, which were also preceded by major emplacement of vent breccias (the vents north of Belig and the Loch na Creitheach vent, Bell, 1966; Jassim and Gass, 1970).

Sudden cauldron subsidence and penetration of magma into country rocks permeated with meteoric water is an ideal situation for locally generating enormous water pressures. This would be expected to produce repeated explosive activity and accompanying formation of breccia pipes and explosion vents filled with volcanic agglomerate (Taylor and Forester, 1971). Thus, explosive fracturing that accompanies formation of volcanic vents might not only provide easier access for meteoric waters to the magma chamber below, but the explosive activity might very likely be caused by the influx of meteoric waters. In this regard, note that the Loch na Creitheach agglomerates and tuffs are made up of some of the most ^{18}O-depleted rocks on Earth. The average $\delta^{18}O_R$ from five separate volcanic vents in Skye is -2.7, and many of these intrusions may have been emplaced as low-^{18}O magmas.

We might therefore tentatively explain the $^{18}O/^{16}O$ relationships shown on figure 10 as follows. During major explosive vent activity, the country rocks and earlier intrusions became intensely fractured, allowing large quantities of ground water to penetrate to great depths. Melting of country rocks or exchange between magmas and meteoric water could then produce low-^{18}O magmas. At an early stage of this process, a given set of magmatic intrusions might decrease slightly in $\delta^{18}O$ with time as did the Early Epigranites of the Western Red Hills. However, as activity proceeds, the originally highly fractured rocks tend to become sealed because of extensive mineral deposition along veins and fractures, thereby decreasing the amount of low-^{18}O H_2O that penetrates into the zone of partial melting or to the upper portions of the magma chambers. This phenomenon should cause the later magmas produced in the zone of partial melting to become progressively enriched in ^{18}O, thereby more

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closely approaching the $\delta^{18}O$ values of "normal" granitic magmas. This could account for the positive trends shown by the Later Intrusions of the Western Red Hills and the early granites of the Eastern Red Hills. These trends should continue until the region undergoes another major explosive brecciation event, or there is a shift to a new zone of cauldron subsidence.

Beinn an Dubhaich Granite (BDG).—The BDG is unique in that it is the only granite in Skye that was emplaced entirely into *carbonate* country rocks. Because of its anomalous occurrence, both in terms of type of country rock and its essentially "normal" $\delta^{18}O$ values (Taylor, 1968; Taylor and Forester, 1971), the BDG was studied in some detail in the present work (figs. 4 and 13). Seven $\delta^{18}O_R$ values for dikes related to the BDG were also measured. The $\delta^{18}O_Q$ values for the BDG are all similar to those of "normal" igneous quartz, whereas the $\delta^{18}O_K$ values cover a wide range, +6.0 to −1.0. Most of the low $\delta^{18}O_K$ values are from fine-grained samples; these are very rare in the BDG, but several examples were studied to determine the $\delta^{18}O$-grain size effect in greater detail.

The results of the quartz and alkali feldspar analyses are plotted in figure 13 as a function of grain size. The most pertinent features shown by this diagram are (A) $\delta^{18}O_Q$ is independent of grain size and restricted to the range +7.8 to +6.9, (B) $\delta^{18}O_K$ is strongly dependent on grain size, and (C) for a given grain size, $\delta^{18}O_K$ is lower for samples near joints, fractures, and dikes than for samples of massive granite. The grain-size relationships apply not only from specimen to specimen but also within a single rock sample. For example, SK-196 is a porphyritic BDG sample, and $\delta^{18}O_Q$ is similar in both the groundmass and phenocrysts, whereas

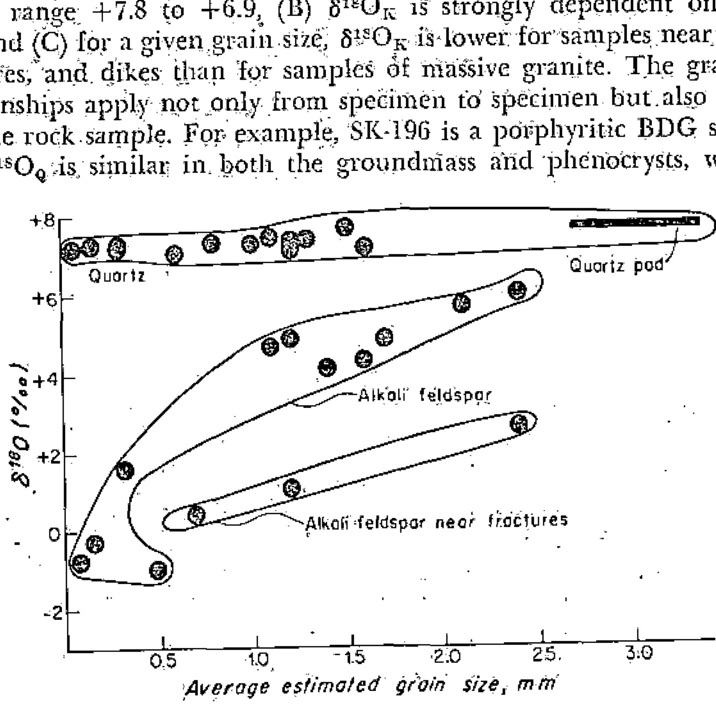

Fig. 13. Plot of $\delta^{18}O$ versus grain size for quartz and alkali feldspar from the Beinn an Dubhaich granite (BDG). Note that the $\delta^{18}O_K$ values that fall off the main feldspar trend represent samples collected along joints in the BDG.

$\delta^{18}O_K$ differs markedly in these two sites. These grain-size effects clearly indicate that the BDG has undergone subsolidus oxygen isotope exchange. It is likely that the grain-size effects show up in the BDG because the W/R ratios were very low. In the other Skye epigranites, the hydrothermal exchange was so pervasive and involved so much H_2O that grain size was not a dominant factor.

The postulated low W/R ratios are consistent with the geologic features of the BDG, which is well removed from all younger intrusions in the area. Thus it may have been affected by only a single stage hydrothermal episode (its own). Also, the Durness Limestone was very likely much less permeable to ground waters than the plateau basalt country rocks (Taylor and Forester, 1971). The carbonate rocks would have been less permeable to H_2O, if, during contact metamorphism and hydrothermal alteration, they deformed plastically or by recrystallization rather than by fracturing. At the physical conditions under which the BDG cooled and crystallized, the strength of dolomite is much less than that of basalt or granite (Griggs, Turner, and Heard, 1960). Any fractures that do form would also tend to be sealed quickly by the hydrothermal fluids, because carbonates are much more easily recrystallized than silicate rocks.

Another important effect may be that the limestone could have acted as a high-^{18}O "buffer", making ^{18}O-depletion difficult. Such carbonate country rocks would provide a localized, easily exchanged, ^{18}O-rich reservoir that would produce much more ^{18}O-rich ground water than would be observed throughout the rest of the Skye intrusive complex. However, this could not have been a dominant effect, because we know that low-^{18}O ground waters did in fact penetrate the BDG, at least in small amounts.

It is significant that each of the three BDG samples collected adjacent to fractures or dikes have $\delta^{18}O_K$ values lower than those of the main BDG trend shown in figure 13. The implication here is that these samples have been in contact with larger amounts of H_2O than those farther removed from these channel-ways; higher W/R ratios would be expected along the fractures.

WATER/ROCK RATIOS IN THE SKYE INTRUSIVE COMPLEX

Just as is the case for the basaltic country rocks, large amounts of meteoric-hydrothermal fluids must have circulated through the Skye plutonic complex. In order to explain $\delta^{18}O_F$ values as low as −7.1 in the Cuillin gabbro with an initial $\delta_{H_2O} = -12$ requires a T ≅ 630°C and W/R ≅ 2.5 (also see table 2). If the H_2O is higher in ^{18}O as a result of prior exchange with the country rocks, then higher W/R ratios are required. For example, if the initial $\delta_{H_2O} = -9$, temperatures lower than 600°C delineate W/R > 5 for the feldspars with $\delta^{18}O = -7.1$, and temperatures lower than 500°C require W/R>>10. The range of W/R values necessary to interpret satisfactorily the $\delta^{18}O$ values of the Cuillin gabbros is approximately 0.3 to 5.0, and at temperatures significantly lower than 500°C, much larger W/R values would locally be required.

The granitic rocks of Skye (excluding the Beinn an Dubhaich granite, discussed below) have $\delta^{18}O_R$ values ranging from +3.1 (BCG, SK-37) to −5.9 (GE, SK-126). The average $\delta^{18}O_R$ value of the whole-rock samples (either measured or calculated from quartz and alkali feldspar $\delta^{18}O$ analyses) is approximately −1. Two-thirds of the rocks are characterized by $\delta^{18}O_R = -1.5 \pm 0.5$. Utilizing a reasonable average temperature on the order of 400° to 500°C, most of the Skye granitic rocks must have experienced time-integrated W/R ratios of approximately 1.0 to 2.0. Locally, however, W/R ratios may have reached very large values (>>5).

The Beinn an Dubhaich granite has an average $\delta^{18}O_R \approx +6.0$. Even if we take into account that the initial δ_{H_2O} may have been greater than −9, this still defines W/R <<1. The alkali feldspar data clearly illustrate that the H_2O that did interact with the BDG was relatively low in ^{18}O, and therefore one cannot appeal to high $\delta^{18}O_{H_2O}$ values perhaps produced by exchange with limestone to argue against the conclusion that low W/R ratios are required for the BDG. This *demands* a fairly impermeable country rock, as only very locally, along fractures, did the W/R ratios approach unity in the BDG.

CONCLUSIONS

The general trend of decreasing $\delta^{18}O$ with decreasing distance from the Skye intrusive complex is clearly shown by the country rock basalts, sandstones, and shales (figs. 1 and 6). The ^{18}O effects extend about 5 km farther outward in the basalts than in the sedimentary rocks, largely as a result of the differences in bulk permeability. Note also that most of the low-^{18}O effects in the country rocks are concentrated in the immediate vicinity of the intrusive complex, just the pattern expected on the basis of both measured and experimentally observed fluid flow patterns in geothermal systems (Elder, 1965).

The dike rocks characteristically have $\delta^{18}O$ values not too dissimilar to the country rocks they intrude. This similarity could come about in either of two ways: (1) The dikes, with normal $\delta^{18}O$ values, were injected into country rocks that also had normal $\delta^{18}O$ values, and simultaneously or subsequently, both types of rocks underwent meteoric-hydrothermal alteration; (2) dikes with normal $\delta^{18}O$ values invaded hydrothermally altered, ^{18}O-depleted country rocks, and the dike magmas exchanged oxygen with the country rocks in a plutonic environment; note that this process may occur essentially independent of meteoric-hydrothermal phenomena, as it has been documented in a wide variety of plutonic environments. It is probable that most of the Tertiary dikes in Skye were intruded along fractures that were former channelways for hydrothermal fluids. In fact, the fluids could have penetrated these fractures at any stage before, during, or after dike emplacement.

The above discussion applies to all the dikes in southern Skye, with the notable exception of those very late-stage dikes cutting the Glas

Beinn Mhor epigranite that have normal or near-normal $\delta^{18}O$ values (fig. 3). These minor intrusions *must* have been emplaced (with normal $\delta^{18}O$ values) into relatively cold country rocks, and thus they represent one of the latest stages in the evolution of the central intrusive complex.

The coexisting minerals in the plutonic rocks of the central intrusive complex are characterized by $\Delta^{18}O$-values that are markedly out of equilibrium. The $\Delta^{18}O_{Q-F}$ and $\Delta^{18}O_{F-P}$ values in particular demand that most of the ^{18}O exchange in these rocks has taken place at subsolidus temperatures. Feldspar is by far the most susceptible rock-forming mineral to oxygen isotope exchange and thus represents a good monitor of the subsolidus exchange process. It apparently exchanges so readily that grain size is ordinarily not an important factor; relationships between $\delta^{18}O_F$ and grain size are not found except in the case of meteoric-hydrothermal exchange involving very small W/R ratios (as exemplified by the Beinn an Dubhaich granite; see fig. 13).

Both gabbroic and granitic plutons show evidence of having been intruded, at least in part, as ^{18}O-depleted magmas. The emplacement of the granitic ring intrusions was accompanied by systematic $\delta^{18}O$ variations as functions of time; these trends can be explained by a simple meteoric-hydrothermal model, which involves both extensive subsolidus exchange and the generation of ^{18}O-depleted melts. The oxygen isotopic discontinuities among the Red Hills granites *all* correlate with significant geologic events in the evolution of the Tertiary intrusive complex, and the $\delta^{18}O$ variations seem to correlate with the igneous and tectonic history of south-central Skye.

The first tangible evidence for the existence of ^{18}O-depleted magmas came from Forester and Taylor (1972) in discussing the Stony Mountain inner diorite. Undeniable evidence of low-^{18}O magmas has since been furnished by Muehlenbachs, Anderson, and Sigvaldason (1974) and Friedman and others (1974) in their studies of recent volcanic rocks. Mechanisms for generating ^{18}O-depleted magmas have been discussed in these papers and by Forester and Taylor (1972) and Taylor (1974a,b). The most likely mechanisms to have operated in Skye are (1) oxygen isotope exchange between the already hydrothermally altered, ^{18}O-depleted country rock and magma, and (2) direct melting of the hydrothermally altered, ^{18}O-depleted country rocks in the roof zone above the magma chamber. Direct diffusion of H_2O into the magmas probably also occurred, but such a process cannot quantitatively account for the large ^{18}O depletions observed. Oxygen isotope exchange between the liquid magma and the hydrothermally altered wall rocks that form a shell around the magma chamber would be facilitated by (A) the high H_2O content of the country rocks, and (B) the fact that the ^{18}O-depleted, turbid feldspars in the country rocks are relatively easily exchanged and thus even more susceptible to a second alteration event (O'Neil and Taylor, 1967). The efficiency of this exchange process depends on the surface-to-volume ratio of the magma chamber and would be enhanced by the presence of low-or near-normal $\delta^{18}O$ values been emplaced (with normal cks, and thus they represent ıe central intrusive complex. rocks of the central intrusive at are markedly out of equi- particular demand that most place at subsolidus tempera- ɔle rock-forming mineral to a good monitor of the sub- ıanges so readily that grain relationships between $\delta^{18}O_F$ se of meteoric-hydrothermal ıs exemplified by the Beinn

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^{18}O xenolithic debris provided by piecemeal stoping of the shattered roof and wall rocks. Note that this process is not necessarily one of wholesale dissolution and assimilation but merely communication and selective exchange between oxygen in the silicate melt and oxygen in the country rocks or stoped blocks (probably mainly the feldspars and hydrous phases). This process can generate ^{18}O-depleted basaltic *or* granitic magmas equally well; evidence for both compositional types has been demonstrated in Skye and elsewhere. Note that in support of the above model the Pb and Sr isotope data of Moorbath and Bell (1965) and Moorbath and Welke (1969) also require major involvement of the country rocks in the magmatic processes.

The other probable exchange model involves partial melting of hydrothermally altered, low-^{18}O country rocks in the roof zone above a magma chamber. These melted rocks could have $\delta^{18}O$ values as low as the average $\delta^{18}O$ values of the altered rocks from which they formed, providing they did not mix with appreciable "normal" magma. The necessary heat may in whole or in part be supplied from the heat of crystallization of early-formed minerals, from supply of new magma in a volcanic conduit to the surface, and/or from another intrusion. Note that Bott and Tuson (1973) have interpreted their gravity survey as indicating that about 3500 km^3 of probable gabbroic material (ρ=3 g cm^{-3}) underlies the plutonic centers of Skye to a depth of approximately 14 km. Magmas produced by partial melting in low-^{18}O terranes would almost certainly be ^{18}O-depleted magmas and would also probably be inhomogeneous in ^{18}O. The $\delta^{18}O$ data on the Southern Porphyritic epigranite support previous models that this magma was derived by melting Torridonian sandstone, and in addition they suggest that this melting was a consequence of the high P_{H_2O} associated with the meteoric-hydrothermal activity.

A significant aspect of the data on some of the Skye granites is the correlation of $\delta^{18}O_Q$ with sequence of intrusion, a relationship similar to that noted by Friedman and others (1974) for sequential eruptions of rhyolites and ash-flow tuffs from Nevada, Colorado, and Yellowstone. These time-dependent trends thus also provide evidence for $\delta^{18}O$-depleted magmas. It should further be noted that at Skye this type of progressive ^{18}O lowering in the magmas seems to be initiated by an explosive breccia event (for example, the Loch na Creitheach volcanic vent, Jassim and Gass, 1970). However, an opposite type of $\delta^{18}O$ versus time relationship is also observed at Skye in association with subsolidus exchange in the feldspars, as well as in certain sequences of granitic intrusions that begin with a change in the center of igneous activity (for example, between the Early Epigranites and the Later Intrusions of the Western Red Hills, and between the Later Intrusions and the Eastern Red Hills granites). This type of $\delta^{18}O$-time trend is probably a result of decreasing hydrothermal activity at depth due to progressive sealing of the fractures by mineral deposition. Such a trend apparently continues until the region undergoes another major explosive brecciation event, or until there is a shift to a new center of cauldron subsidence.

ACKNOWLEDGMENTS

We thank S. Epstein, L. T. Silver, and S. M. F. Sheppard for valuable discussions of this work. S. M. F. Sheppard kindly helped us collect some of the samples, and John Esson, Ros Todhunter, Anne Bateman, and Steven Moorbath generously contributed others. Sam Epstein made available certain laboratory facilities, and Paul Yanagisawa did some of the laboratory work. This research was principally supported by National Science Foundation Grants GA-12945 and GA-30997X; additional support came from the Phelps Dodge Fund and the National Research Council of Canada Grant A8698.

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