Hydrothermal Sr contamination of the Dippin sill, Isle of Arran, Western Scotland

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ABSTRACT. The Dippin sill, which is emplaced into the Triassic sediments of SE Arran, is an alkaline basic sheet which displays pronounced hydrothermal alteration. The 40-m-thick sill has suffered pervasive contamination with radiogenic Sr, introduced from the Triassic sediments by hydrothermal fluids. Stable isotope measurements suggest that fluids were of meteoric origin, but were restricted to a small closed-system circulation. Initial $^{87}Sr/^{86}Sr$ ratios in the sill were raised from an original value of 0.7032 to a maximum of 0.7091, contamination being especially pronounced near the contacts at Dippin Head itself (localities 12 and 14) and in a drill core section through the sill above Dippin. Hydrothermal Sr was incorporated into an early-formed high-CaO, high-Sr analcime, which replaced unstable high-silica nepheline in interstitial patches. However, this high-CaO analcime, along with plagioclase, was later replaced by a low-CaO, low-Sr analcime, allowing Sr leaching from the margins of the sill. Hydrothermal fluids are thought to have migrated up to 1 km laterally, up the dip of the sill, mainly via tension joints forming in the cooling intrusion. Pooling of hot fluids at the upper end of the sill probably raised water/rock ratios in this region and allowed greater Sr contamination during mineralogical alteration. The undersaturated mineralogy of the sill accounts for its pervasive hydrothermal Sr contamination, which contrasts markedly with the relatively undisturbed Sr isotope compositions of Hebridean granites involved in hydrothermal systems.

THE Dippin sill is a large, 40-m-thick, alkaline basic sheet of gentle dip which is intruded into Triassic sediments in SE Arran (fig. 1). Gibb and Henderson (1978) made a detailed study of the petrology and geochemistry of the sill, based mainly on two

exposed sections and two drill core sections. Major element analysis of suites through the whole thickness of the sill led them to suggest that the margins of the intrusion had been contaminated with sedimentary material. They attributed this contamination to a combination of bulk sediment assimilation by the magma, and the introduction of material by a fluid phase under sub-solidus conditions. In this study, we attempt to test this model by means of Sr, O, and H/D isotope measurements, and to examine fluid pathways in the sill.
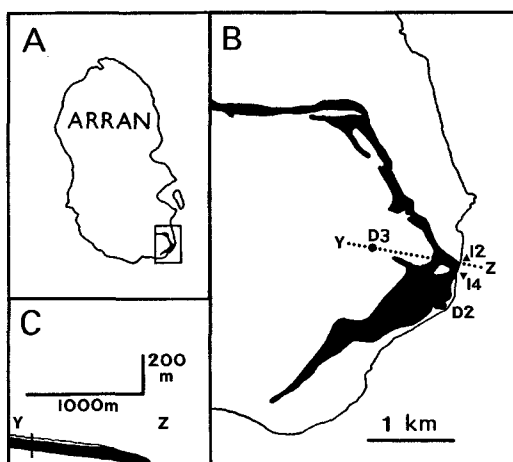

FIG. 1. Maps showing the locality of the Dippin sill in Arran. Localities 12 and 14, and the position of drill holes 2 and 3 are shown in fig. 1B (these were the same as used by Gibb and Henderson, 1978).

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Petrography. Alteration of the primary mineralogy is very marked at the margins of the Dippin sill, but decreases somewhat inwards. The centre of the intrusion has a sub-ophitic texture, with abundant fresh clinopyroxene; plagioclase has undergone some alteration to chlorite, serpentine, and zeolites, particularly along fractures; rounded grains of olivine display variable degrees of serpentinization; and wedge-shaped interstices between the primary igneous minerals are filled by analcime.

The grain size of the rock decreases gradually towards the lower contact, becoming very fine at the chilled margin. Plagioclase alteration increases towards the margin, until replacement is almost complete 5 cm from the contact. Alteration of pyroxene to serpentine and chlorite also becomes significant near the margin, while olivine is completely replaced, so that alteration products make up the bulk of the rocks near the contact. Interstitial analcime contents increase from the centre of the sill towards the marginal teschenite zone (Gibb and Henderson, 1978) in the locality 12 section, but fall off again in the chilled margin (Dickin, 1980), probably due to reduction in grain size eliminating the spaces between plagioclase laths. The upper contact has a similar chilled margin, but grain size increases rapidly within a few decimetres of the contact. Zeolite-filled veins are fairly common throughout the sill, but no internal chilled margins (an indicator of multiple intrusion) were observed within the sill despite almost 100% drill core recovery.

Major element chemistry. In fig. 2, selected major element oxide data for drill core 3 and locality 12 samples (Gibb and Henderson, 1978; Dickin, 1980; and unpublished data) are plotted against height above the lower contact of the sill. Both sections show similar trends of enrichment of K_2O, Na_2O, and SiO_2, and depletion of CaO, in the marginal teschenite zone within about 1.5 m of the lower contact. Similar trends may be present near the upper contact of the drill core 3 section, but these are partially obscured by erratic compositional variations associated with a pegmatitic zone observed by Gibb and Henderson.

Gibb and Henderson attributed MgO and CaO enrichments in the centre of the sill to the intrusion of magma enriched in olivine and plagioclase phenocrysts by flow differentiation in the feeder conduit. They suggested that the marginal teschenites represented a more differentiated magma, which developed additional compositional variation due to inward enrichment of pyroxene (again by flow differentiation) and also contamination by sedimentary wallrock, either by bulk assimilation or selective enrichment via a fluid phase.
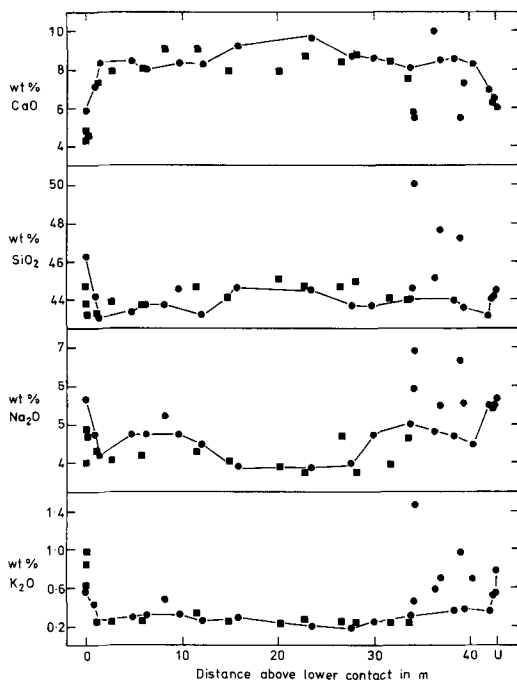
Marginal silica enrichment in fig. 2 can easily be

FIG. 2. Profiles of selected major element oxides plotted against distance from the lower contact in m. (■) = locality 12; (●) = drill core 3.

explained by bulk assimilation of sediment by the earliest intruded magma, which would tend to line the conduits and shield later magma from such contamination. However, the increase in Na_2O near the contacts can only be explained by fluid action, since the sediments contain less Na_2O than the sill itself. Thus, fluids could have selectively leached Na from the country rocks and deposited it in the margin of the sill. Although the sediments contain substantially more K_2O than the sill, the enrichments at the lower contact (fig. 2) are well above those which could be produced by sediment assimilation without causing excessive silica enrichment, and it is argued that these K-enrichments are also best explained by hydrothermal processes.

CaO depletion at the lower contact is problematical. It could be a product of magmatic differentiation caused by plagioclase or pyroxene fractionation, since the differentiated top of a stratified magma chamber will tend to be tapped first (Blake, 1981), but could also be explained by hydrothermal leaching. On a plot of CaO versus MgO (fig. 3), plagioclase, olivine, and clinopyroxene crystallization vectors show that correlated MgO and CaO variations in the centre of the sill can be explained by magmatic fractionation
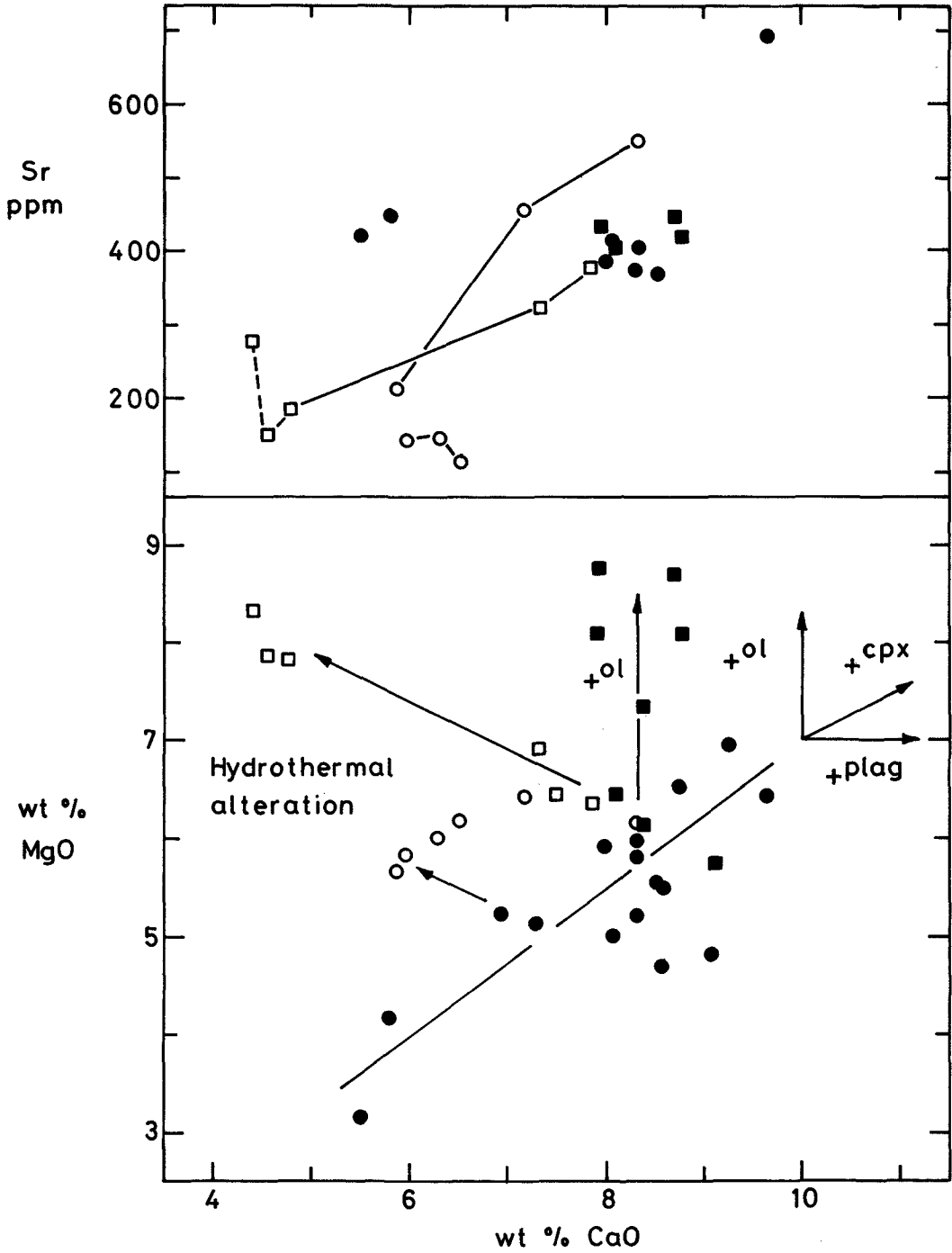
FIG. 3. Variation diagrams of MgO and Sr against CaO content. Open symbols = marginal teschenites; solid symbols = crinanites, pegmatites, etc. (□, ■) = locality 12; (○, ●) = drill core 3.

TABLE I.

Sample	Rock Type	Distance from Contact	Rb ppm	Sr ppm	Y ppm	Zr ppm	$\frac{^{87}Sr}{^{86}Sr}$	$\frac{^{87}Rb}{^{86}Sr}$	$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{60}$
Triassic sandstone									
72/24 (Loc.12)		- .02	58.1	103	9	274	0.72589	1.64	0.72449
AC329 (core 2)		- .45	54.2	98	9	217	0.72352	1.60	0.72216
AC439 (core 3)		- .25	119	255	15	614	n.d.		
Locality 12, whole-rocks (distances from lower contact)									
72/26a	MT	.03	14.2	279	36	187	0.70444	0.16	0.70430
72/26b	MT	.05	12.7	181	36	188	0.70433	0.21	0.70415
72/26c	MT	.10	17.5	151	36	184	0.70517	0.35	0.70487
72/28	MT	1.1	5.5	327	31	166	0.70449	0.06	0.70444
72/29	MT	2.6	5.6	377	33	159	0.70443	0.05	0.70438
72/31	CR	5.8	4.3	408	29	150	0.70409	0.04	0.70406
72/36	CR	14.8	5.4	393	26	n.d.	0.70386	0.05	0.70382
72/41	CR	20.1	4.3	437	27	152	0.70361	0.04	0.70358
72/44	CR	22.7	4.3	447	27	146	0.70367	0.03	0.70364
72/59a	PG	28.3	5.9	419	44	n.d.	0.70415	0.05	0.70411
72/23	MT	36.4	6.6	231	43	n.d.	0.70622	0.09	0.70614
Locality 14, whole rocks (distances from upper contact)									
72/86	MT	.02	16.3	135	38	n.d.	0.70610	0.37	0.70578
72/85	MT	.20	13.2	176	41	n.d.	0.70582	0.23	0.70562
72/84	MT	.56	6.7	278	37	n.d.	0.70617	0.08	0.70610
72/83	MT	.92	7.2	202	44	n.d.	0.70580	0.12	0.70570
72/81	MT	2.4	5.9	240	37	n.d.	0.70491	0.08	0.70484
72/71	CR	10.7	5.1	426	38	n.d.	0.70379	0.04	0.70376
72/91	AT	20.1	4.1	250	30	n.d.	0.70436	0.06	0.70431
Drill core 3, whole-rocks and mineral separates (distances from upper contact)									
AC451Z	MT	.02	9.7	313	3	n.d.	0.70920	0.10	0.70912
AC453	MT	.23	12.8	148	32	177	0.70655	0.27	0.70632
AC455PX	MT	.61	2.5	70	73	n.d.	0.70378	0.15	0.70365
AC455Z	MT	.61	8.4	275	11	n.d.	0.70783	0.10	0.70775
AC490	CR	3.8	12.3	416	56	374	0.70556	0.09	0.70548
AC542	PG	8.5	18.4	570	84	536	0.70755	0.10	0.70747
AC543PX	PG	8.7	2.0	176	n.d.	n.d.	0.70478	0.03	0.70475
AC649	CR	19.4	4.7	693	29	141	0.70590	0.02	0.70588
AC699Z	CR	28.7	16.7	167	2	n.d.	0.70722	0.30	0.70696
AC807	MT	42.1	8.5	475	28	157	0.70663	0.06	0.70658
AC809B	MT	42.7	15.2	186	34	183	0.70705	0.25	0.70684
Locality 12, Leachates in excess cold 2.5M HCL									
72/26bL							0.70739	1.01	0.70653
72/26cL							0.70750	0.52	0.70706
72/26cL (repeat)							0.70753		
72/28L							0.70556	0.11	0.70547
72/29L							0.70558	0.22	0.70539
72/41L							0.70483	0.20	0.70456
Locality 12, Residues after leaching with hot aqua regia									
72/26bR							0.70393	0.15	0.70380
72/26cR							0.70423	0.34	0.70394
72/26cR (repeat)							0.70421		
72/28R							0.70356	0.04	0.70353
72/29R							0.70338	0.06	0.70333
72/41R							0.70325	0.05	0.70321

n.d. = Not determined. Z = zeolite, PX = pyroxene

MT = marginal teschenite, AT = augite teschenite, CR = crinanite, PG = pegmatite.

of these phases. However, the inverse correlations of MgO and CaO which are observed towards the contacts can best be explained by hydrothermal alteration. Enrichment in MgO and depletion in CaO result from replacement of the primary olivine–pyroxene–plagioclase mineralogy by a secondary hydrous assemblage with abundant chlorite. This process was observed by Whyte (1960, 1980) and Dickin and Whyte (1983) at the contact of the Dumbarton Rock basalt.
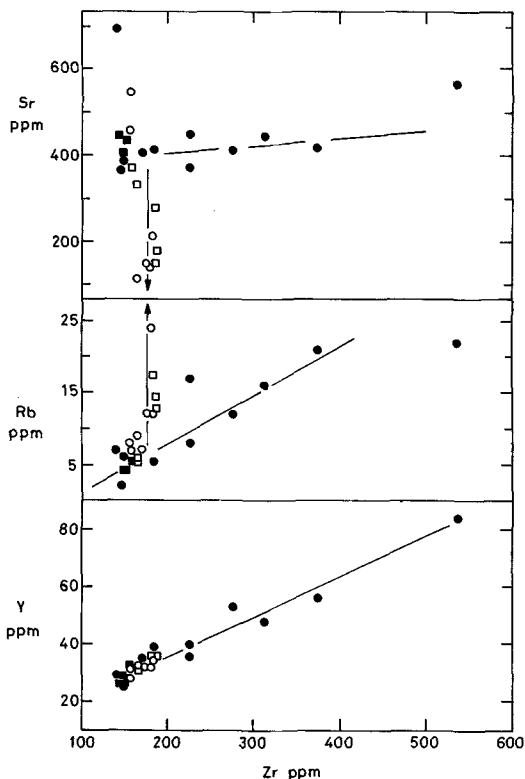

FIG. 4. Variation diagrams of trace elements plotted against Zr content. Symbols as in fig. 3.

Trace element chemistry. Selected trace element contents (Table I) are plotted against Zr in fig. 4. Y and Zr are two incompatible elements (in a basaltic mineralogy) which are widely recognized as being relatively immobile during hydrothermal metamorphism (e.g. Pearce and Cann, 1971; Vallance, 1974; Wood et al., 1976). Concentration of olivine and plagioclase in the centre of the sill does not appear to have strongly affected the concentrations of these elements, since the range for marginal teschenite samples (open symbols) overlaps with that of the interior. Similarly, the incorporation of

Triassic sediment cannot have significantly affected trace element abundances, since its large Zr contents (217–614 ppm) and low Y contents (9–15 ppm) would tend to cause a displacement of compositions towards the bottom right in fig. 4, which is not observed. It is concluded that the good correlation of Zr and Y must be due to magmatic differentiation, which causes substantial incompatible element enrichments in the pegmatite zone.

Most samples from the interior of the sill yield a similar positive correlation between Zr and Rb (fig. 4), which is ascribed to magmatic differentiation. Sr contents in these samples average 440 ppm (± 40 ppm, 2 SDM) and do not correlate strongly with Zr. The presence of large stellate plagioclase growths in the centre of the sill suggests that this was an early fractionating phase along with olivine, and since Sr is moderately compatible in plagioclase, this must have held Sr to a nearly constant level.

Samples from the marginal teschenites define very steep trends of Rb enrichment and Sr depletion at nearly constant Zr content (fig. 4). These trends are attributed to the action of hydrothermal fluids in introducing Rb and leaching out Sr from the sill margins. This interpretation is supported by the strong correlation between CaO and Sr contents in the marginal rocks (fig. 3). The slight enrichment of Zr and Y observed near the lower contact at locality 12 may be a combination of relative enrichment due to the hydrothermal leaching of other elements (e.g. Dickin and Jones, 1983), and a slight dilution effect in the centre of the sill due to the concentration of Y- and Zr-poor olivine and plagioclase phenocrysts.

Sr isotope chemistry. Initial $^{87}Sr/^{86}Sr$ ratios (Table I) are plotted in fig. 5 against relative height in the sill. For drill core 3 this is a fraction of the total sill thickness (42.8 m). For the locality 12 and 14 sections the total thickness (39.6 m) was estimated from correlation of the thin pegmatite horizon and the top of the crinanite unit (Gibb and Henderson, 1978, fig. 4).

Whole-rock samples from the locality 12 and 14 sections show similar patterns of isotopic ratio against height. Initial $^{87}Sr/^{86}Sr$ ratios are low in the centre of the sill (minimum = 0.7036) but rise as high as 0.7049 near the lower contact at locality 12 and 0.7061 near the upper contact at locality 14. The uppermost sample from locality 12 also has an initial ratio of 0.7061, consistent with it being from close to the contact. It seems that only c. 3 m of sill are missing from the top of the locality 12 section, and that, as at locality 14, no thick pegmatite zone is present in the eastern part of the Dippin sill.

Crinanite and teschenite whole-rock samples from drill core 3 show similar trends of initial ratios, but displaced to higher values than localities 12 and
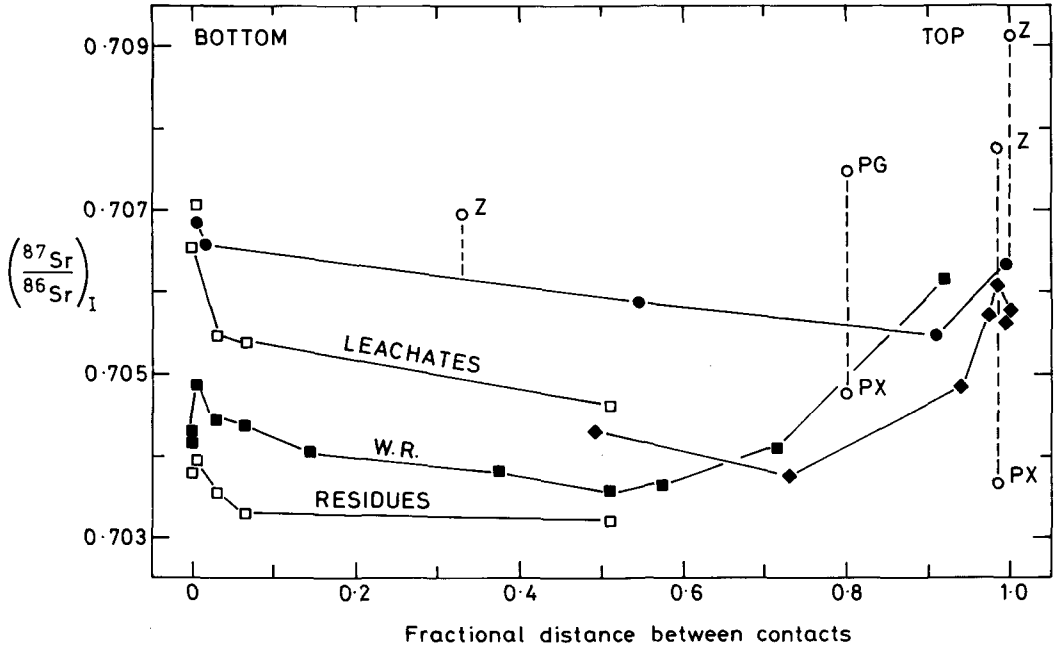
FIG. 5. Initial Sr isotope ratios plotted against the fractional distance between lower and upper contacts of the sill. Solid symbols = whole-rock data; (■) = locality 12; (♦) = locality 14; (●) = drill core 3; PG = pegmatite. Open symbols = mineral separates, etc. Z = zeolite; PX = clinopyroxene.

14. Initial ratios range from a minimum of 0.7059 in the centre to a value of 0.7068 at the lower contact, but the highest whole-rock composition (0.7075) is in the pegmatite zone.

Whole-rock samples of Triassic sandstone from near the lower contact at locality 12 and drill hole 2 (fig. 1) have similar but quite radiogenic $^{87}Sr/^{86}Sr$ ratios at 59 Ma, averaging 0.7232. Thus the high initial ratios near the contacts at localities 12 and 14, and throughout drill core 3, are attributed to contamination of low $^{87}Sr/^{86}Sr$ magma or rock with radiogenic crustal Sr, probably derived from the Triassic sediments. In order to determine whether this isotopic contamination occurred at the magmatic stage or was caused by a sub-solidus influx of hydrothermal fluids, the whole-rock samples were tested for internal initial isotopic heterogeneity.

The relatively coarse grain-size of the rocks near the upper contact in drill core 3 allowed the separation of clinopyroxene and zeolite fractions from the marginal teschenite AC455. These fractions display substantial initial isotopic heterogeneity, with ratios of 0.7037 for the pyroxene and 0.7078 for adjacent zeolites. Since the pyroxenes are essentially unaffected by hydrothermal activity, the ratio of 0.7037 is interpreted as the original isotopic

composition of the magma at this point in the sill. The high initial ratio for the zeolites separated from AC455 is consistent with the composition of a zeolite vein from nearer the top of the sill in drill core 3 (AC451Z; initial ratio = 0.7091) and a zeolite patch from a central crinanite of drill core 3 (AC699Z; initial ratio = 0.7070). Thus the radiogenic initial isotope ratios of these zeolites represent a minimum value for the composition of hydrothermal fluids carrying large quantities of contaminating Sr derived from the Triassic sandstones. Therefore, at the upper contact, by far the greater proportion of Sr isotope contamination of the whole-rocks must have been introduced by hydrothermal fluids after magmatic crystallization.

The fine grain-size of samples near the lower contact of the sill makes mineral separation difficult, so a leaching procedure was used for samples from the locality 12 section. The secondary hydrothermal minerals, serpentine, chlorite, and zeolite, are more soluble in acid than primary plagioclase and pyroxene, so the leachates give a minimum $^{87}Sr/^{86}Sr$ ratio for the hydrothermal fluids, while the residues give a maximum value for the isotopic composition of the magma. Leachate initial ratios increase from 0.7046 in the centre of the intrusion up to 0.7071 near the lower contact, while residues

have ratios as low as 0.7032 in the centre of sill, rising to a maximum of 0.7039 near the lower contact. These results suggest that even the whole-rock sample near the centre of the sill (A72/41) has suffered a small degree of hydrothermal contamination to raise the initial ratio from 0.7032 to 0.7036. Nevertheless, contamination at both the magmatic *and* hydrothermal stages appears to have been greater at the contact. The marginal material, representing the first injection of magma into the crust, would be expected to display stronger effects of any magmatic Sr contamination than the centre of the sill, which was protected from contact with the wall rocks by the chilled marginal envelope. It is worth noting at this point that the deduced primary igneous composition at the lower contact of locality 12 (A72/266R; 0.70380) is practically within analytical error of that at the upper contact of drill core 3 (AC455PX; 0.70365).

The generally higher whole-rock $^{87}Sr/^{86}Sr$ ratios of the crinanites from drill core 3 (fig. 5) suggest a greater degree of contamination by radiogenic Sr, compared with crinanites from equivalent levels in the sill at the locality 12 and 14 sections. The pegmatite from drill core 3 (AC542) appears to have

suffered the greatest degree of contamination, much of which occurred during hydrothermal alteration. However, significant contamination must have occurred at the magmatic stage, because a pyroxene separate (leached with aqua regia) has a comparatively high initial ratio of 0.7048. It seems likely that hydrothermal fluids entered the sill before crystallization of the pegmatite zone was complete, and contaminated the residual magma.

Stable isotope chemistry. Levels of combined water (H_2O+) tend to increase from the centre of the sill towards both margins (fig. 6), suggesting a substantial influx of fluids from the country rocks. $^{18}O/^{16}O$ and D/H measurements were made in an attempt to identify whether these fluids were of meteoric or connate origin. The results (Table II) are plotted in fig. 6, showing that $^{18}O/^{16}O$ and D/H ratios are similar in whole-rock samples from the sill centre, chilled margin, and Triassic sandstone lower contact rocks at locality 12, and in a pyroxene separate from near the upper contact in drill core 3. In contrast, zeolites from the latter locality have distinct compositions which could be due to the presence of different zeolite species with contrasting mineral/water fractionation factors.
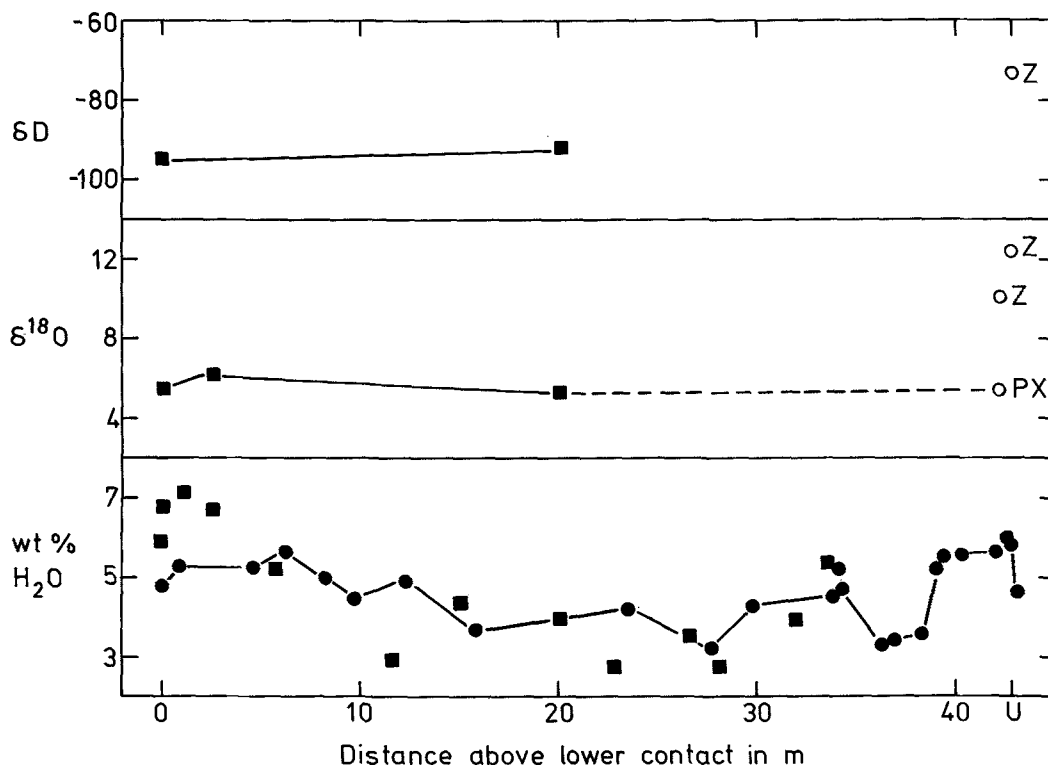

FIG. 6. Water contents, $\delta^{18}O$ and δD plotted against distance through the sill. Symbols as in fig. 5.

Table II

Sample No.	Sample Type	$\delta^{18}O$	δD
72/24	SED	+ 4.43	- 98.0
72/26b	MT	+ 4.45	- 94.9
72/26c	MT	+ 5.45	n.d.
72/29	MT	+ 6.19	n.d.
72/41	CR	+ 5.31	- 92.2
455 PX	cpx	+ 5.37	n.d.
455 Z analcime		+ 10.01	n.d.
455 Z[1] + natrolite		+ 10.28	n.d.
451 Z vein - laumontite?		+ 12.04	- 73.3

[1]Sample baked at 120°C before reaction

n.d. = not determined.

On the δD versus $\delta^{18}O$ diagram (fig. 7) the compositions of the sill rocks and adjacent sandstone lie close to the field for normal pristine basic igneous rocks, but are displaced downwards by 10–15 parts per mil δD and 1 part per mil $\delta^{18}O$. The composition of a granitic whole-rock from the Central Ring Complex of Arran is shown for reference (unpubl. data). The latter has suffered ^{18}O depletion to $+1.1\%$ and contains moderately

abundant epidote, both of which can be explained by pervasive interaction with meteoric fluids. Since the hydrogen reservoir of a rock is much smaller than its oxygen content, D/H exchange with fluids may be almost complete before $^{18}O/^{16}O$ exchange becomes significant. Hence increasing water/rock ratios produce a hyperbolic curve on the D/H versus $^{18}O/^{16}O$ plot (Taylor, 1977). Such a curve can be drawn in fig. 7, through the compositions of Dippin sill rocks and Central Ring Complex granite, suggesting that the Dippin sill probably exchanged oxygen and D/H with small amounts of ground water similar to that which affected the central granite. The pervasive nature of Sr isotope contamination in the intrusion indicates that there was ample opportunity for complete D/H and $^{18}O/^{16}O$ exchange between fluids and the sill, so the small degree of ^{18}O depletion observed must be explained by limited *access* of meteoric water to the convection system set up round the sill.

Calculations by Jaeger (1957) indicate that the centre of a sill 40 m thick would cool from 1200 °C to < 600 °C in *c.* 55 years by conduction alone. However, cooling by convection of hydrothermal fluids in a super-critical sheath around the sill could speed this up by two orders of magnitude (J. W. Elder, pers. comm.). The hydrothermal convection system set up by intrusion of the Dippin sill therefore probably lasted only a few years, and is
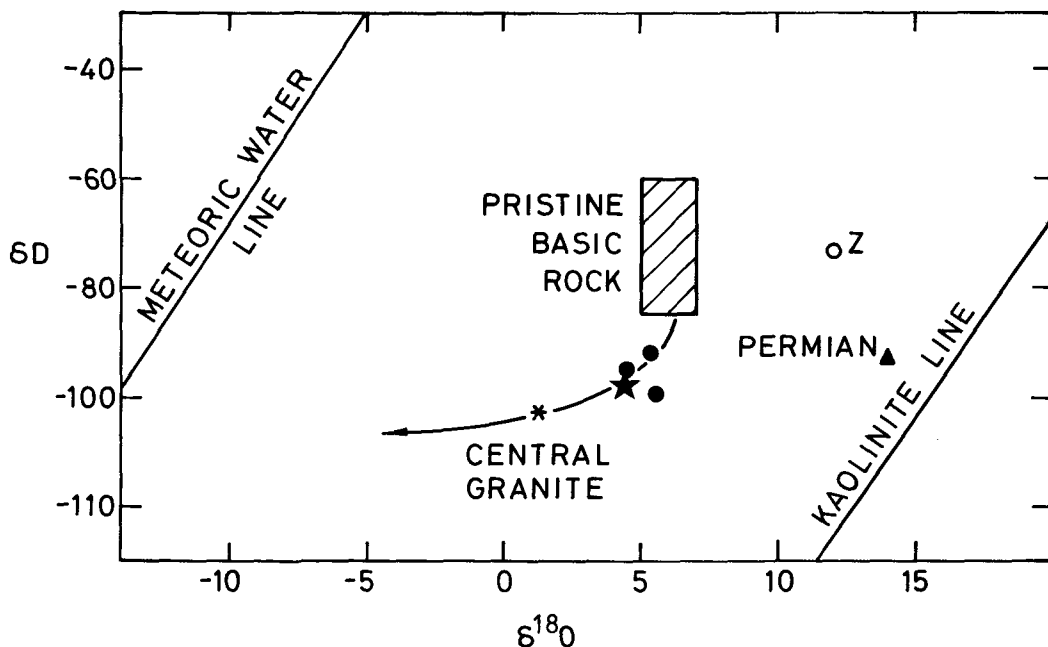

FIG. 7. δD versus $\delta^{18}O$ plot for Dippin sill rocks. (★) = Triassic sandstone near lower contact; (▲) = Permian sandstone P3 from W. coast of Arran (Dickin et al., 1981); CRC = Central Ring Complex granite.

unlikely to have grown sufficiently large to reach the lower Tertiary land surface. In this situation, the ground water reservoir available was large enough to buffer the D/H sites in the sill, but not its $^{18}O/^{16}O$ composition. On the contrary, the $^{18}O/^{16}O$ composition of country rocks immediately adjacent to the sill (e.g. A72/24) was more or less buffered *by* the sill, and within the intrusion isotopic homogenization was achieved.

The stable isotope data cannot rule out a contribution to the ground-water system by connate formation water, since the δD value of unaltered Permian sediment on Arran is within error of the Dippin sill δD compositions. Nevertheless, the oxygen isotope compositions of this and other sediments from Arran are much richer in ^{18}O than the Dippin sill, so that exchange of oxygen between the country rock silicates and the sill can be ruled out.

Exchange mechanisms. It was argued above from elemental evidence that the margins of the Dippin sill were depleted in Sr by hydrothermal leaching, but isotopic evidence points to the *introduction* of sedimentary Sr into the sill margins by hydrothermal fluids. This amounts to a process of two-way movement, or Sr exchange between the sill and hydrothermal fluids, similar to that observed in the Coire Uaigneich Granophyre and Sconser quarry basic sill of Skye (Dickin *et al.*, 1980; Dickin and Jones, 1983) and the Dumbarton Rock basalt (Dickin and Whyte, 1983).

In order to elucidate the mechanisms of Sr exchange in the Dippin sill, it is important to establish whether hydrothermal Sr leaching pre-dated, post-dated, or was simultaneous with Sr introduction. These alternatives can be tested using a simple mixing model in which Sr contamination is attributed to a fluid phase containing Sr with the same isotopic composition as adjacent Triassic sandstone as the only dissolved species. The limited extent of fluid-induced major element contamination observed suggests that this is a fairly good approximation to the natural system. Using a simple mass balance equation, the amount of Triassic Sr introduced into each whole-rock is defined as follows:

Added Triassic Sr in ppm =

$$C \times \frac{\frac{^{87}Sr}{^{86}Sr_I} - 0.7032}{0.7232 - 0.7032}.$$

Where C = the Sr content of the rock after contamination.

By putting C equal to the presently observed Sr contents, the case where contamination post-dated Sr leaching can be modelled. The results (fig. 8A)

predict that the margins of the sill would have suffered substantially *less* sedimentary Sr addition than the core of the intrusion. In previous studies of hydrothermal exchange (e.g. Smith and Giletti, 1979; Dickin *et al.*, 1980; Dickin, 1983; and Dickin and Whyte, 1983) the margins of intrusive units were observed to suffer greater degrees of contamination than the core, so this model seems unlikely.

It was noted above that Sr contents in the interior of the sill average 440 ppm. If this value is taken to be the Sr concentration at the time of contamination, and inserted as C into the mixing equation, then the case where hydrothermal leaching post-dated contamination can be modelled (fig. 8B). These results show low degrees of contamination in the centre of the sill at localities 12 and 14, rising to higher degrees at the lower, and especially upper, contacts, while drill core 3 displays high degrees of contamination throughout. These patterns are more consistent with the results of hydrothermal studies cited above, than those calculated for model A. Sr leaching simultaneous with contamination would produce intermediate results between models A and B, and hence would still yield a degree of contamination for the lower contact of drill core 3 less than that for the interior. It is therefore concluded that Sr depletion from the margins of the Dippin sill largely post-dated contamination.

For the whole Dippin sill to have suffered marked Sr contamination in a few years, hydrothermal fluids must have infiltrated along grain boundaries and tension fractures which developed in the cooling intrusion. Fracture and grain boundary fluids would only be partially buffered by the surrounding mineralogy, and would remain as a system at least partially open to Mesozoic sedimentary Sr throughout the sill. In this situation the degree of Sr isotope contamination suffered by different parts of the sill may have depended almost entirely on the degree of Sr exchange between individual mineral grains and the grain boundary fluid. Solid state diffusion would have been far too slow to have a significant effect in a few years, so Sr contamination must have resulted from mineralogical recrystallization during alteration.

Henderson and Gibb (1977) showed that interstitial analcime in the Dippin sill was not a primary igneous mineral but a secondary hydrothermal alteration product. They attributed its formation to the hydration of interstitial nepheline, which was particularly susceptible to alteration, because of its high SiO_2 content. Gibb and Henderson (1978) suggested that the first-formed interstitial analcime was relatively rich in CaO (up to 1.8 wt. %), and new microprobe analyses reveal 200-400 ppm Sr in
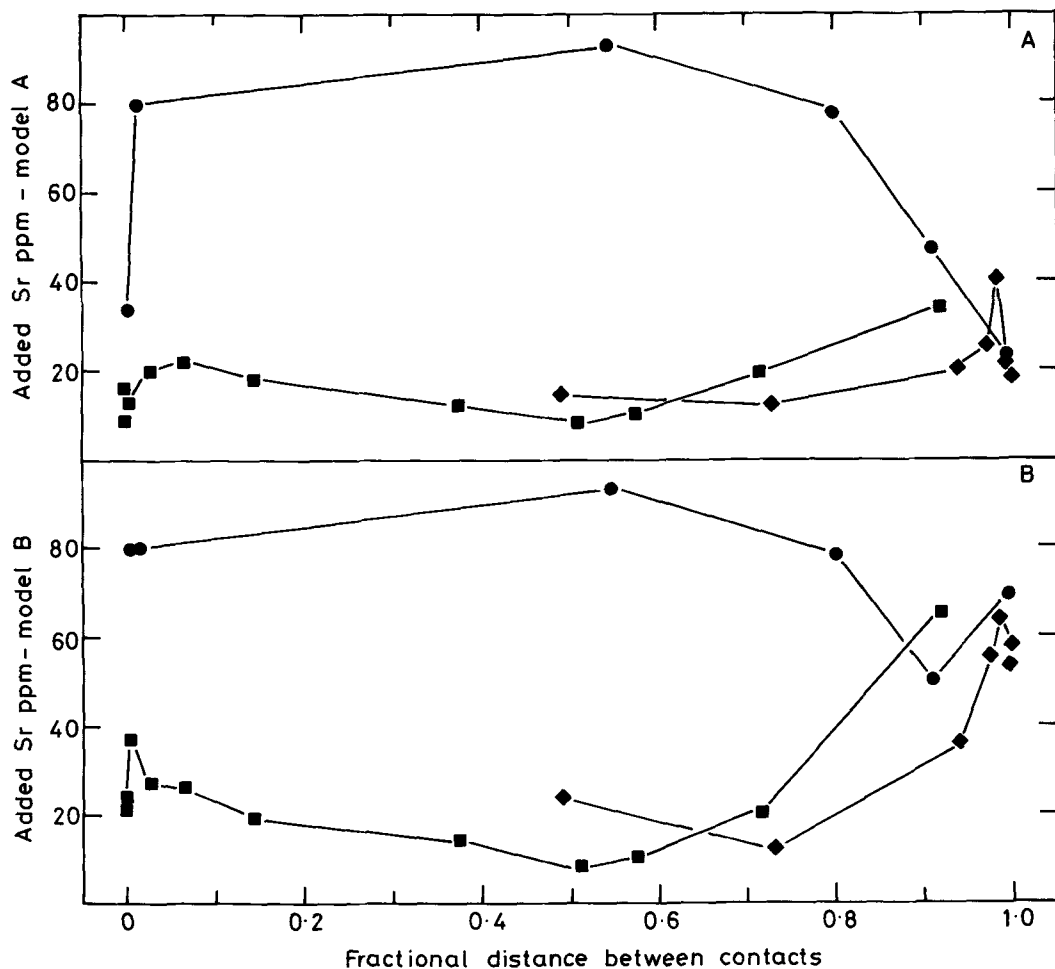
FIG. 8. Profiles of calculated sedimentary Sr additions plotted against fractional distance between the contacts for models A (contamination after leaching) and B (contamination before leaching). Symbols as in fig. 5.

these grains. The formation of this CaO-rich analcime by metasomatism in a fluid phase would tend to incorporate radiogenic sedimentary Sr which had entered the sill in hydrothermal fluids.

Petrographic and microprobe observations suggest that the early high-CaO analcimes altered subsequently to low-CaO analcime with Sr contents below 50 ppm (probe detection limit), associated with natrolite and an occasional Ca-rich zeolite. It appears that plagioclase laths suffered alteration along internal cracks at this stage, again yielding a low-CaO analcime (fig. 9) with Sr contents below 100 ppm. Chlorite and serpentine, formed by alteration of olivine and pyroxene, were also ineffective at taking up Sr from hydrothermal fluids (Dickin and Jones, 1983) in view of their

alternating sheet structure of silica and small cations. Thus it appears that the main site for Sr contamination of the Dippin sill was an interstitial Ca-rich analcime formed at c. 350 °C (Henderson and Gibb, 1977). Subsequently, lower temperature hydrothermal processes then allowed leaching out of Sr and its redistribution between other zeolite species. The smaller degree of contamination observed in the chilled margins at localities 12 and 14 (figs. 5 and 8) may be due to the lower interstitial analcime contents observed in these rocks.

Fluid pathways. The generally higher whole-rock initial $^{87}Sr/^{86}Sr$ ratios and consequently greater amounts of added sedimentary Sr in drill core 3, relative to the locality 12 and 14 sections, may be related to absolute altitude in the sill. The sill dips
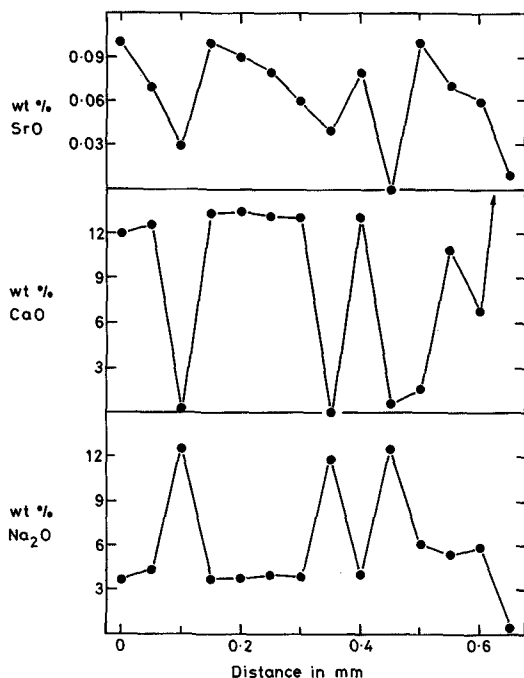
FIG. 9. Microprobe step scan determinations along an altered, fractured plagioclase lath, sample 72/41.

gently to the east by about 6° (Gibb and Henderson, 1978) and the top of the sill in drill hole 3 is some 110 m higher than at locality 14. The horizontal attitude of the Mull and Antrim Tertiary lava piles demonstrates that the Hebridean province has not undergone any major tectonic disturbance in the last 60 Ma, and therefore suggests that the present dip represents the original attitude of the Dippin sill.

After solidification and the formation of cooling joints, water probably entered the intrusion at its lowest point near localities 12 and 14 and, after heating, rose to the upper contact. Impermeable shaly bands in the sediments may have obstructed the escape of fluids into the overlying country rocks, so that they were constrained to migrate up dip within the sill. If the escape of hot fluids was restricted at the upper end of the sill above drill hole 3, then the whole intrusion would have tended to saturate with hot water from the top downwards, in the same way as oil collects in an aquifer. The high temperatures and water/rock ratios prevalent in the vicinity of drill hole 3 probably resulted in substantial formation of the high-CaO analcime, so that incorporation of sedimentary Sr from the fluids was enhanced. The absence of the main pegmatite zone from the studied sections other than

drill core 3 may indicate that its formation depended on the upward concentration of hydrothermal fluids in this part of the sill.

The model described above implies lateral flow of hydrothermal fluids for 1 km or more in the upper part of the Dippin sill. This is analogous to the model of Hawkesworth and Morrison (1978) for Sr isotope contamination of Mull lavas, in which the vesicular upper parts of lava flows provided a preferred pathway for lateral movement of hydrothermal fluids within the lava pile.

The significance of Sr contamination in the Dippin sill. The pervasive nature of isotopic contamination suffered by the Dippin sill contrasts strongly with the limited extent of hydrothermal Sr exchange which was observed in the Tertiary epigranites of Skye. In the Coire Uaigneich Granophyre (CUG), contamination was restricted to material within 1.5 cm of veins (Dickin et al., 1980). This contrast is even more remarkable when it is noted that hydrothermal activity in the Dippin sill probably only lasted a few years, while the CUG was subjected to the Cuillins hydrothermal convection system for tens of thousands of years (Dickin, 1981a).

The origin of these striking contrasts can be ascribed to the differing mineralogy of the two intrusions: the CUG is a siliceous granite, while the Dippin sill was originally an olivine dolerite containing an unstable high-silica nepheline. Most Sr in the CUG is contained in feldspars, of which plagioclase is most susceptible to hydrothermal alteration, but even this only became albitized and exchanged Sr within 1.5 cm of hydrothermal veins, where fluid/rock ratios were very high. The 'armouring' effect of a high modal quartz content probably helped to protect CUG plagioclase from alteration. In contrast, the unstable nepheline of the Dippin sill was almost totally replaced throughout the intrusion, and the alkalis released by the alteration processes would have promoted cation exchange and further alteration in the remaining nepheline, olivine, and plagioclase (O'Neil and Taylor, 1967).

The high degree of Sr contamination of the Dippin sill is therefore a consequence of its alkaline mineralogy, and contrasts with the low degrees of hydrothermal Sr contamination suffered by silica-oversaturated rocks such as Hebridean granites.

Analytical techniques. Isotopic analyses were carried out on whole-rock samples, on magnetically separated pyroxene and zeolite, on the products of leaching with cold dilute HCl and on residues after leaching with hot aqua regia. Rb/Sr ratios were measured for leachates and residues in addition to the other samples, in order to make age corrections to the estimated age of 60 Ma (Dickin *et*

al., 1981). For age corrections on leachates and residues to be accurate, dissolution of Rb and Sr must involve the complete breakdown of certain minerals, rather than selective removal of certain elements from a crystal structure which remains intact. In an attempt to test this assumption, a repeat leaching procedure was carried out on sample A72/26c. The excellent agreement between $^{87}Sr/^{86}Sr$ ratios for both leachate and residue in the two leaching runs suggests that a fundamental threshold in mineral dissolution was reached, rather than a transient stage in selective trace element extraction. Even if this assumption is not fully upheld, age corrections are generally so small (less than 0.0003 for whole-rocks and residues) that errors from this source are unlikely to exceed uncertainties of $^{87}Sr/^{86}Sr$ measurement and cannot effect the conclusions. $^{87}Rb = 1.42 \times 10^{-11}$ (Steiger and Jäger, 1977).

Rb and Sr in leachates and residues were determined by mass spectrometric isotope dilution (Dickin and Exley, 1981). Other trace element measurements were made by X-ray fluorescence using USGS standards (Dickin, 1981b). Accuracy is estimated to be 0.5 ppm or 3 % (2σ), whichever is the larger.

Sr isotope ratios were measured on a VG Micromass 30 mass spectrometer at Oxford using routine procedures (Dickin, 1981b). $^{87}Sr/^{86}Sr$ ratios are corrected to a value of 0.70800 for the Eimer and Amend Sr standard. Within run precision averages 0.00004 (2σ).

O isotope ratios were measured on an automatic VG Micromass 903 mass spectrometer at East Kilbride. Oxygen was extracted from rock powders by a modification of the technique of Clayton and Mayeda (1963) using Cl F_3 reactant (Borthwick and Harmon, 1982), after baking of powders at 200 °C to drive off unbound water. $^{18}O/^{16}O$ ratios are reported in the δ notation relative to SMOW, using the Snowbird Quartz ($+16.20\%$) and African Glass Sand ($+9.60\%$) standards. The reproducibility of standards run in the course of this work was $\pm 0.8\%$ (2σ).

D/H ratios were determined on a VG Micromass 602 mass spectrometer at East Kilbride. Hydrogen was extracted from evolved water in a U furnace at 900 °C, and collected using a Töppler pump. Results are reported in δ notation relative to SMOW, and reproducibility is estimated to be $\pm 4\%$.

Microprobe step scan measurements were made on a Cambridge Scientific Instruments Microscan 9 electron microprobe with a beam current of 5×10^{-8} A focused to a spot. The accelerating voltage was 20 kV.

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