

Carbonate enrichment at the margins of a basic dyke, Ardnamurchan

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SUMMARY. A gradational increase in concentration of CO_2 towards the margins of a very fine-grained basalt dyke has led to the development of a pale marginal facies, enriched in carbonates, particularly siderite. Increases in CO_2 from about 3 % in the interior of the dyke to 8 % at the margins are accompanied by decreases in SiO_2 and Fe_2O_3 , increases in Al_2O_3 , and less significant changes in the other major components. Cu, Co, and Zn change only slightly, and Cr, Ni, and Li remain constant. Petrographic variation is considerable, even in the superficially homogeneous interior of the dyke, in which it ranges from a type containing a titanite (analysed) to one devoid of pyroxene, but containing conspicuous opaque minerals. Microprobe analysis for Fe and Ti shows that these comprise: octahedral titaniferous magnetite; rodlets, less than $1 \mu\text{m}$ thick, of rutile partly altered to, or overgrown by, ilmenite; and sub-opaque patches with a very low Ti/Fe ratio. Plagioclase, An_{55} , is the most abundant and constant crystalline phase in the interior of the dyke, but changes to An_{20} in the marginal facies. Mineral-content of the latter, deduced from optical, chemical, and X-ray data, also includes siderite, serpentine and clay minerals, leucocoxene, and apatite. There is no evidence of quartz, sericite, or calcite.

Petrographic evidence shows that variations in concentrations of CO_2 and H_2O affected phase equilibria from the start of magmatic crystallization. Data on the $f\text{O}_2$ required for TiO_2 and Fe-oxide phases to co-exist at magmatic temperatures indicate that, initially, the concentrations of CO_2 and H_2O in the interior of the dyke were higher than the values recorded in analyses of the rocks. From this evidence and the field relationships, it is concluded that the intruding magma was rich in volatiles, which diffused towards the dyke margins and, in part, became trapped as the magma congealed, producing a changed marginal assemblage of minerals. The dyke provides a unique glimpse of influences on a basic magma exerted by what S. J. Shand has aptly termed the 'fugitive constituents', the transient effects of which are rarely preserved in the rocks.

THE dyke outcrops below high water mark about 50 m east of the Sròn Bheag headland on the south of the Ardnamurchan peninsula, west of Kilchoan (1 in. Ordnance Survey Sheet 45, map reference 465623). Credit for finding the dyke and recognizing that it possessed features of particular interest must go to Dr. J. E. Richey. When he showed it to one of us (M. K. W.) in 1948, it was assumed from the field evidence, unsupported at that time by any laboratory study, to be a very unusual kind of composite intrusion in which the normal roles of the acid and basic components had somehow been reversed, so that the acid member occurred at the margins. This seemed quite likely in view of the proximity of the dyke to the Sròn Bheag so-called 'composite intrusion', in which a massive body of dolerite is flanked on both sides by felsites (Richey and Thomas, 1930). An opportunity to make a thorough examination of the dyke did not arise until 1971; but even then it was not until samples had been chemically analysed that it was realized that the marginal rock is, in fact, more *basic* than the main part of the dyke, due to an abundance of carbonate minerals.

Field relationships

The dyke has an approximately SW.–NE. trend, which is roughly parallel to the local cone-sheets and at right angles to the regional dyke swarm (fig. 1). It is steeply inclined at angles of $70\text{--}5^\circ$ to the NW., i.e. in the same direction as the cone-sheets, though the latter dip at about 40° or less. It is continuously exposed over a distance of 35 m of rocky foreshore, outcropping between two small inlets in which the rocks are

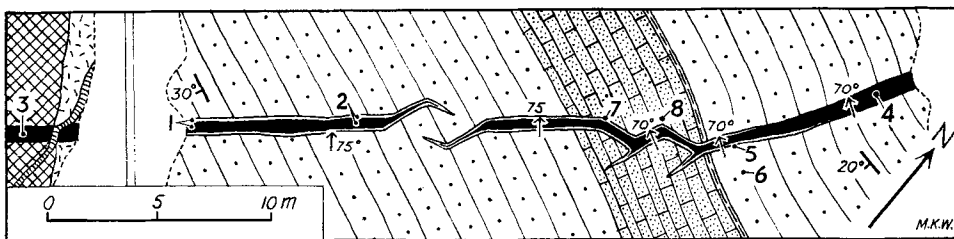


FIG. 1. Map showing specimen localities and the intrusive relationships of the dyke to Jurassic strata (see text) and to the felsite (dashed) and dolerite (cross-ruled) members of the Sròn Bheag 'composite' intrusion. A 20 m gap separates the two parts of the outcrop. Eastward extension of the dyke beyond the pebble beach (blank) is not shown. Note that care is needed to distinguish the later dyke, shown on the map (cross-ruled), from the apophyses of the carbonated dyke.

covered by beach pebbles. It reappears, however, at the NE. end, cutting a thick dolerite dyke belonging to the regional swarm, and at the SW. end, being traceable for several metres across the felsite and into the massive quartz dolerite of the Sròn Bheag composite intrusion. In the main part of the outcrop, the dyke cuts across strata of Inferior Oolite age, which show a gently undulating dip of between 20° and 30° to the SW.

Amongst features visible in the field that are regarded as critical concerning the marginal carbonation, are:

1. A pale marginal facies, up to 10 cm in width, occurs on both sides of the dyke and extends very uniformly and apparently without break throughout the western half of the outcrop. Towards the eastern end of the outcrop the marginal facies becomes gradually less conspicuous.
2. Although development of the marginal facies is obviously governed by proximity to the contacts, it is apparently quite independent of the character of the immediately adjacent country-rocks.
3. The marginal facies extends into apophyses of the main dyke, with widths that are scaled down in proportion to the dimensions of the latter.
4. Transition from the main, central part of the dyke to the marginal facies is in general gradational, as shown in fig. 2.
5. Where the dyke is intruded into dolerites at each end of the outcrop, marginal variation, apart from chilling, is entirely absent.

Because of their very fine-grained character, the rocks can only be distinguished in the field on the basis of their colour, which broadly reflects their carbonate-content.

The real extent of variation can only be appreciated by a combination of microscopic examination and chemical analysis. This shows that considerable variations in concentrations of H_2O , in addition to the more obvious CO_2 , occurred in different parts

of the dyke during its consolidation and that *both* exerted significant effects on the mineral content and texture. The combined evidence shows that variation exists within the superficially homogeneous interior of the dyke, as well as between this and the marginal facies.

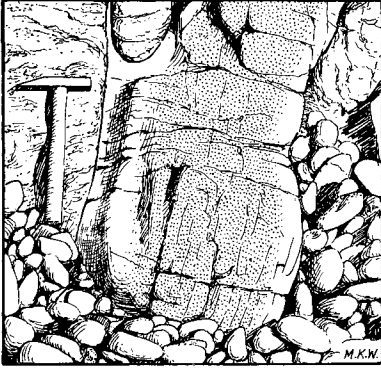


FIG. 2. The western end of the outcrop where the dyke intrudes sediments, drawn from the photograph to show the gradation from the interior (stippled) to the marginal facies. Note that the gently inclined surface of the outcrop presents virtually a plan view. Samples 1A and 1B were collected from the left-hand side of the dyke, near the hammer head.

carbonation is well developed. This is petrographically similar to the first type as far as plagioclase is concerned; but pyroxene is only sparsely developed, and highly distinctive forms of opaque oxide minerals are conspicuous.

The pale beige-coloured, marginal facies (Type 3), comprising crystals of plagioclase that are more sodic than in Types 1 and 2, set in a matrix that is exceedingly finely, but completely, crystallized, notably deficient in opaque ores, and in which cloud-like aggregates of minutely granular carbonates are the only components that can be identified with any confidence.

Type 1. Sample 4, illustrated in fig. 3, is typical of varieties containing appreciable amounts of pyroxene. It is a very fine-grained and sensibly aphyric rock in which the only easily identified components are minute crystals of plagioclase and generally subordinate pyroxene. These are set in a matrix that is partly glassy, but mostly composed of exceedingly fine-grained to cryptocrystalline aggregates of minerals that largely defy identification. As can be seen from fig. 3, opaque minerals are not abundant and consist mostly of minute, slightly rounded grains, which may occur in isolation, but sometimes in small, compact aggregates. In addition, some of the glassy patches are so densely charged with iron ore dust that they may become opaque. Graticules of ore rodlets also occur in very small amounts. Since the opaque minerals assume much greater importance in the rocks of Type 2, they are described below under that heading.

Petrography

Figs. 3, 4, and 5 show the characteristics of the three main varieties that can be distinguished petrographically:

Fairly normal-looking basalt (Type 1) containing plagioclase and appreciable amounts of a titaniferous augite as the main crystalline phases, set in a partly glassy matrix. This type occurs towards the eastern end of the outcrop where the dyke cuts the Jurassic strata, and at the eastern and western limits where the dyke cuts earlier dolerites.

A paler, grey variety (Type 2), occurring in the centre of the dyke where the marginal

The plagioclase forms glassy clear, prismatic crystals, which may be up to 0.1 mm long and about 0.01 mm wide. Some of them are skeletal. In most crystals only two twin units are visible, but the bigger crystals show multiple lamellae.

Extinction angle measurements indicate compositions of about An_{55} . Very sparse phenocrysts of plagioclase also occur throughout the dyke: the section of Sample 4 is typical in containing two such phenocrysts. In the main these are euhedral with sharply defined margins. They had obviously crystallized before the magma was intruded, since they are all between about 50 and 100 times the size of the second-generation crystals. U-stage measurements suggest that the phenocrysts have high-temperature optics, with compositions in the range An_{55} to An_{62} .

The most distinctive feature of this rock type is the relative abundance of a single phase of clinopyroxene, which occurs in simple {110} prismatic crystals. These are commonly skeletal, with irregular terminations and incompletely crystalline cores. As shown in fig. 3, the crystals are generally arranged in radial aggregates. They show fairly strong absorption and are weakly pleochroic in tints of pinkish brown and mauve.

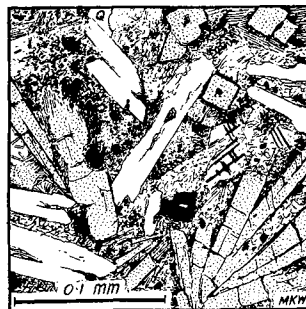


FIG. 3. Petrography of Type I, represented by Specimen 4, showing clear laths of plagioclase and radial aggregates of titanaugite, with both minerals exhibiting features of skeletal growth. Note the finely disseminated magnetite, sparse occurrence of rutile/ilmenite rods, and the indication of an indeterminate, fibrous mineral associated with the pyroxene.

TABLE I. Analysis of titanaugite from Sample 4

	Weight %	Atomic proportions	
SiO ₂	48.78	Si	1.855
TiO ₂	2.76	Al ^{IV}	0.145
Al ₂ O ₃	4.72	Al ^{VI}	0.067
*FeO	11.42	Ti	0.079
MgO	10.42	Fe	0.363
CaO	20.41	Mg	0.591
Na ₂ O	0.75	Ca	0.832
K ₂ O	0.09	Na	0.055
		K	0.004
		Mg	33.1
Total	99.35	Fe	20.3
		Ca	46.6

* Total Fe expressed as FeO. Electron microprobe analysis by J. F. W. B.

The average of corrected analyses of five separate crystals show a TiO₂-content of 2.76 % (Table I). This is slightly less than any of the pyroxenes listed as titanaugites by Deer, Howie, and Zussman (1963, p. 123), the nearest of whose analyses relates

to a titanaugite from a teschenite in Poland containing almost the same amount of TiO_2 (2.42 %), less SiO_2 (44.71 %), and more Al_2O_3 (7.85 %).

This rock-type and the next one to be described provide obscure indications of the presence of a colourless, fibrous mineral, which has moderate birefringence and straight extinction. Occasional fibres may extend for 1 mm or more, though generally the aggregates are so poorly defined and so masked by inclusions that they can barely



FIG. 4. Petrography of Type 2, represented by Specimen 1A, showing clear laths of plagioclase, sparse pyroxene (p), rutile and ilmenite rods, magnetite crystals, and dark-brown, almost opaque iron-rich patches which merge into the general matrix. This matrix is partly glassy, but poorly crystalline mica (top right) and microgranular patches of carbonate minerals (e.g. bottom right) can be distinguished with difficulty.

be discerned. No estimate can be made of the abundance of this phase, which may possibly be an amphibole and is mentioned here because in some instances the fibres are parallel with, and adjacent to, the pyroxenes. Sample 3 contains appreciably less pyroxene than 4, but in the matrix contains some chloritic patches, which are absent in 4.

Type 2. Specimen 1A, illustrated in fig. 4, is representative of the second type, and comes from the central part of the dyke at the western end of the main outcrop (see fig. 2). Although the plagioclase is closely similar to that of Type 1, in other respects the two types are very different. Titanite is very sparsely and inconspicuously developed and the two crystals ('p') shown in fig. 4 happen to be the only ones found in the slide. Opaque minerals are relatively abundant and form the most conspicuous feature of the rock when viewed under high magnification. They and the tiny plagioclase crystals are set in an abundant matrix of dusty grey-brown material, which is probably in the main glassy, but

shows patchy, incipient birefringence. In part the latter can be shown to be due to a pale brown, pleochroic mica, and in part to carbonate minerals.

The oxide minerals occur in two distinct phases. The first takes the form of a graticule of orientated rodlets, developed in three mutually perpendicular directions. In general, any particular domain of the matrix between plagioclase crystals tends to be occupied by a single graticule. It should be noted that the apparent volume of this phase is much greater than the real volume owing to the fact that the opaque rods are so thin (of the order of $1 \mu\text{m}$) that they occupy only a small fraction of the thickness of the rock-slice. This is also responsible for the marked reduction in the amount of the ore phase visible on a polished surface, and for the low totals obtained by microprobe analysis (Table II). The other oxide phase comprises euhedral crystals of magnetite up to about 0.03 mm diameter, some of which show skeletal growth. The crystals occur, sometimes in clusters, very commonly adjacent to the plagioclase. The magnetite crystals are sometimes associated with dark brown to opaque patches of the matrix, which are shown by microprobe analysis to be iron-rich. Small quantities of pyrite are also present in Sample 1A.

Microprobe analysis for Ti and Fe was made of areas representative of the

different modes of occurrence of the opaque minerals (Table II). The Ti:Fe ratios in the rodlets are well in excess of those in ilmenite, and in one case the ratio is high enough (9.3) to suggest a composition approaching pure rutile. A triaxial arrangement of the acicular crystals is compatible with their having formed initially as rutile. Ramdohr

TABLE II. *Microprobe analyses of Ti-Fe oxides in Type 2 rock*

Rodlets			Octahedral crystals			Brown cloudy areas		
Weight %		Atomic ratio	Weight %		Atomic ratio	Weight %		Atomic ratio
Ti	Fe	Ti/Fe	Ti	Fe	Ti/Fe	Ti	Fe	Ti/Fe
13	11	1.4	6	20	0.35	0.2	18	0.013
12	8	1.8	4	22	0.21	0.6	16	0.044
16	8	2.3	6	28	0.25	0.4	30	0.016
16	2	9.3	6	23	0.30	0.2	19	0.012

(1969, p. 985) states that ilmenite may replace rutile, often forming crusts and leaving a core of rutile. It is suggested that something of this kind occurred in the present case, causing the rodlets to become opaque.

Type 3. Sample 1B, from the western end of the main outcrop, is representative of the marginally carbonated facies and is illustrated in fig. 5. Conditions of crystallization must have been radically different from those obtaining for Types 1 and 2, since plagioclase crystals superficially resembling those described above constitute the only feature that the rocks have in common. On closer inspection, even the plagioclase turns out to be very different. The crystals are on average smaller, due primarily to the rate of cooling, but partly as a result of alteration. Crystal faces are no longer sharply defined, but merge in an irregular fashion into the microgranular to cryptocrystalline matrix. All evidence of twinning has disappeared and the crystals show straight extinction and have refractive indices only very slightly higher than Canada balsam (1.54).

These properties are consistent with the plagioclase having changed to oligoclase with a composition of about An₂₀. The very occasional phenocrysts found in the marginal rocks show similar features.

Apart from the feldspars, the rock is composed entirely of microgranular and cryptocrystalline aggregates in which the grain-size rarely exceeds 1 μ m. A clear distinction can be made between dark and light patches of the matrix. The appearance of the former is due mainly to the surface relief of granular aggregates of carbonate minerals. Consideration of the chemical composition shows that siderite must be an important

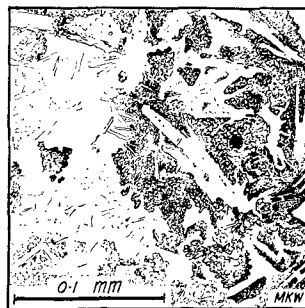


FIG. 5. Petrography of Type 3, represented by Specimen 1B, showing the patchy distribution of the high-relief areas rich in siderite and the low-relief areas. Note the effects of partial alteration accentuating the skeletal structure of some plagioclase crystals.

carbonate constituent, while X-ray diffraction indicates that calcite is absent. It has not been possible to confirm whether or not 'epidote' is present. Minute grains of opaque ore are sparsely distributed through some of the darker areas. The light areas are generally perfectly transparent and colourless, and composed of aggregates of low-relief minerals whose identity is extremely doubtful. In part the cryptocrystalline aggregates appear to be spherulitic, and are either isotropic or show extremely low birefringence, suggesting the presence of serpentine. Other components probably include clay minerals. Evidence for these components is derived partly from the chemical composition (Table III) and partly from X-ray diffraction. The latter shows that quartz is absent.

As shown in fig. 5, the distribution of the various kinds of aggregates is irregular in detail, and as far as can be judged, bears no direct relationship to the texture and distribution of the various phases seen in the less carbonated rocks. For this reason it seems wise to avoid reference to 'alteration' in describing the carbonate-rich rocks. It seems just as likely that the high concentration of CO_2 influenced the course of crystallization from its earliest stages, so that the present mineralogy and textures are to some extent alternatives to, rather than alteration products of, those found in the less carbonated rocks.

Interaction with adjacent sedimentary rocks

Several lines of evidence suggest that the CO_2 and other volatiles must have been dissolved in the magma in depth, and that the carbonation is caused by a marginal concentration of volatiles due to localized physical conditions obtaining during the period of intrusion and consolidation. One item of evidence seems, at least at first sight, to be contradictory. This is the fact that the marginal carbonation is developed only where the dyke is in contact with the sedimentary rocks. Not only is the carbonation missing where the dyke intrudes the Sròn Bheag dolerite, but as shown in Table III, the CO_2 -content (Sample 3) is much lower here than in the other samples.

It is therefore necessary to examine the contact sedimentary rocks critically, to see to what extent they may have contributed CO_2 to the dyke.

The local succession (fig. 1) comprises mainly pale-brown, thickly bedded sandstones. Samples 5 and 6 (Table III) are typical and were from a horizon in the lower part of the succession, the former being in contact with the dyke and the latter 1 m distant. The specimens appear virtually identical in the field, except immediately adjacent to the dyke, where Sample 6 is bleached and weathered to a silvery grey for a thickness of about 1 cm. In thin-section the rocks are seen to be well sorted and compacted quartzofeldspathic sandstones with evidence of recrystallization, shown by sutured grain boundaries. Siderite fills most of the limited space between the grains in both rocks, but whereas in Sample 6 this is accompanied by sparse sparry calcite, in Sample 5 near the dyke the amount of siderite is greater and there is no sparry calcite.

Samples 7 and 8, which have not been analysed chemically, are from a dark-brown, careous-weathering layer, under 1 m thick, which occurs higher in the succession (see fig. 1). This is a distinctly calcareous sandstone in which separated detrital grains are set in an abundant sparry calcite cement containing recrystallized relics of shell

fragments, oolith-like grains, and micrite pellets. In part of Sample 7, immediately adjacent to the dyke, much of the calcite appears to have been replaced by siderite, causing iron staining, and with recrystallization, which leaves incompletely filled voids.

Therefore, for up to 1 cm adjoining the dyke in both lithologies, the calcite cement has been affected and partially replaced by siderite. Some alteration is to be expected, in view of the concentration of hot carbonic acid that must have existed near the dyke margins. However, the extent of the alteration seems in no way commensurate with the extent of carbonation in the dyke. In particular, it is significant that the carbonation is no different in contact with the most richly calcareous sandstone than it is elsewhere.

It is concluded that the magma did not acquire any appreciable amount of CO_2 by reaction with the sedimentary rocks that are seen in the outcrops. This does not exclude the possibility of such reactions having occurred at greater depths. It is worth noting in this connection that the sandstones described above are underlain by thick limestones, which are faulted against the sandstones and outcrop a short distance to the east (Richey, 1930, p. 34).

Chemical variation

Initially, chemical investigation was confined to the analysis of paired samples (1A and B, 2A and B) from the interior and marginal facies of the dyke, the former containing about 50 % SiO_2 and nearly 3 % CO_2 and the latter distinctly less SiO_2 and 8 % or more CO_2 . The analytical programme was extended to cover Sample 4 because of its relatively large pyroxene-content, and Sample 3 because it was suspected that this rock might contain the lowest concentration of CO_2 , since it is furthest from the carbonated margin. As noted in the petrographic section, the pyroxene-rich rock contains a similar amount of CO_2 to 1A and 2A and, in fact, is all but identical with 2A, except in regard to H_2O .

Sample 3 contains only 0.35 % CO_2 and, although this is by far the lowest value amongst the analysed rocks of the dyke, it is still high in comparison with typical fresh basalts. Analysis 3 must, however, be taken to represent the closest approach to the composition of the original dyke magma.

The presence of a titaniferous augite suggests that the magma had somewhat alkali affinities. This appears to be contradicted by the relatively high value of 'hypersthene', over 21 %, which appears in a CIPW Norm that also contains nearly 5 % quartz and about 0.5 % corundum. These figures are, of course, quite unreal in relation to the actual mineral composition and must correspond to the chlorite and mica, and to other components that cannot be determined in the groundmass. They are quoted merely to show that the composition of the magma, even as deduced from the rock containing the lowest percentage of CO_2 , was somewhat unusual.

It is interesting to note that the total-alkali/silica ratio of the Sròn Bheag rock plots exactly on the dividing line between the alkali and tholeiitic suites of Hawaii (Macdonald, 1968). It compares quite closely in composition with a so-called 'low-Fe mugearite' (No. 980) belonging to the Main Lava Series of Skye (Thompson *et al.*, 1972), except that the latter contains more alkalis (4.21 % Na_2O and 2.51 % K_2O). A significant result of the intensive chemical study of these lavas has been to show that,

while most are fairly typical of an alkali-suite, others—including the mugearite noted above—belong to a slightly divergent series, varying from basalt to trachyte, involving the appearance of hypersthene in the norm.

TABLE III. *Chemical analyses of the rocks*

	3	4	1A	1B	2A	2B	5	6
SiO ₂	50·81	49·59	51·03	42·29	49·72	45·76	82·65	75·68
TiO ₂	2·26	2·04	0·88	0·95	1·97	2·18	0·27	0·17
Al ₂ O ₃	16·90	17·89	13·35	15·50	17·94	21·90	3·30	2·36
Fe ₂ O ₃	1·66	0·89	1·30	0·10	0·96	0·01	1·74	1·28
FeO	8·79	9·23	10·85	12·20	9·28	9·91	0·90	0·13
MnO	0·17	0·18	0·16	2·77	0·15	0·13	0·06	0·06
MgO	4·14	3·57	3·07	2·98	3·65	2·16	0·41	0·08
CaO	6·40	7·97	5·31	4·04	7·28	3·71	3·29	7·42
Na ₂ O	2·90	1·97	3·02	3·50	2·02	3·50	0·13	0·13
K ₂ O	1·60	1·73	2·54	2·00	1·85	2·04	0·40	0·43
P ₂ O ₅	0·40	0·39	1·70	2·02	0·39	0·47	0·57	0·33
CO ₂	0·35	2·87	2·66	8·44	2·96	8·00	5·98	11·98
Total H ₂ O	3·56	2·00	4·00	3·27	3·00	1·04	1·64	0·40
SO ₃	n.d.	n.d.	0·88	0·53	n.d.	n.d.	n.d.	n.d.
Total	99·94	100·32	100·86	100·59	101·17	100·91	101·34	100·45

The values for the trace elements analysed, expressed in ppm, are:

1A Cu 86 Co 44 Cr 30 Ni 25 Li 65 Zn 115 Cd < 0·5

1B Cu 60 Co 59 Cr 30 Ni 25 Li 65 Zn 126 Cd < 0·5

Sample numbers refer to the location map, fig. 1.

Although the chemical evidence is inconclusive, on balance it seems likely that the somewhat abnormal composition of the dyke-magma may be linked in origin with the relatively high concentration of volatiles as seen in sample 3 and that the chemical characteristics originated from processes operating at considerable depth.

Although SiO₂ remains fairly constant away from the carbonated margins, the corresponding Al₂O₃ values show considerable variation; the marginal facies show increases relative to the interior of the dyke. Total iron oxides vary very little, though the proportions of Fe₂O₃ fall dramatically in the marginal rocks. This, in fact, is the biggest percentage change of all, reflecting the substitution of siderite for magnetite. Since the percentage of TiO₂ increases in the marginal rocks, it must be assumed that leucoxene is present. Rather surprisingly, P₂O₅ remains fairly constant from core to margin, though it varies along the length of the dyke. The most inconsistent feature of the analyses is the ten-fold increase in MnO in 1B by comparison with the other rocks.

Discussion

One of the most interesting features of the Sròn Bheag dyke is the evidence it provides of the effects of varying concentrations of CO₂ and also, to an important extent, of H₂O, during the intrusion and consolidation of basic magma. The formation of carbonate minerals in basic rocks by late-stage processes, or secondary alteration involving low-temperature solutions, is commonplace and occurs in a variety of

geological environments. However, examples of high-temperature carbonate development seem to be rare.

The distribution and gradational character of the carbonated margins make it seem certain that the volatile components were dissolved in the magma at some depth. Evidence is inconclusive concerning the source and manner of incorporation of the CO_2 . It is possible that, in the initial stage of dilation of the dyke as it penetrated the Jurassic strata, the earliest fraction of magma may already have become enriched in volatile components, and better fluxed, by comparison with the bulk of the magma injected later. However, the gradation between the interior and marginal facies generally seems too perfect for such a process to have operated. Certainly, there is no question of the dyke being in any sense composite, with any time interval between injection of the two facies. It is therefore concluded that the CO_2 and H_2O were able to diffuse in some way through the melt, before the latter congealed. The reason for the diffusion of CO_2 towards the margins of the dyke is unknown. Conditions were obviously changing rapidly, and only a transient combination of circumstances allowed the CO_2 to be retained at its present concentration in the margin of the dyke.

It is envisaged that, under slightly different circumstances (e.g. at shallower depths or with slower cooling), a very high temperature gas phase might have been generated, richer in CO_2 than in H_2O . Tazieff (1970) and his co-workers have shown that, under conditions where air and ground-water contamination are minimal, gases emitted at temperatures of 900 °C or more, from very hot fumaroles, such as the Bocca Nuova on Etna, are composed of CO_2 in excess of H_2O . We are tempted to think that the Ardnamurchan phenomena provide an unusual glimpse of volcanic gases of just such a character becoming trapped at the point where they were about to be evolved from the magma.

From the variations in chemical composition and mineral constitution in all parts of the dyke that are now exposed, it is apparent that phase equilibria were subject to change from the earliest stages of crystallization, due to the varying concentrations of CO_2 and H_2O .

Tentative conclusions relating to this point can be drawn from the evidence of the oxide phases. The appearance of separate iron oxide and TiO_2 phases at an early stage in crystallization indicates the volatile-rich nature of the magma at this time. At an arbitrary temperature of 1100 °C, an olivine+pyroxene+magnetite assemblage is in equilibrium at an oxygen fugacity of about $\log f\text{O}_2 = -8$ (Speidal and Nafziger, 1968). Separation of iron-titanium oxide phases requires more oxygen to be available; thus, at the same temperature, the breakdown of ilmenite into separate oxides requires an oxygen fugacity of $\log f\text{O}_2 = -5.7$ (Verhoogen, 1962a). These figures may be compared with the oxygen fugacity of pure water, which at this temperature and atmospheric pressure is $\log f\text{O}_2 = -4.4$ (Verhoogen, 1962b) and the range $\log f\text{O}_2 = -5$ to -7 quoted for magmatic gas by Kennedy (1948). It seems probable that, at this temperature, the oxygen fugacity of the gaseous phase was about $\log f\text{O}_2 = -5$. Since the early-formed rutile is mantled by ilmenite, it would appear that, at a later stage in crystallization, the volatile constituents were less significant. It appears probable that the iron is present in the form of siderite and it is possible

to link this high oxygen fugacity with the carbon dioxide fugacity using the work of Holland (1959). It requires extrapolation to use the data given by Holland at 1100 °C, but as an approximation this is permissible. The appropriate reactions involve converting magnetite or hematite into siderite and, if the oxygen fugacity of $\log f_{\text{O}_2} = -5$ is accepted, then a carbon dioxide fugacity of about $\log f_{\text{CO}_2} = +7$ results from either reaction. This represents a considerable availability of carbon dioxide during crystallization, of which the 3 to 8 % remaining in the rock is probably only a fraction.

Even allowing that more experimental data on silicate-H₂O-CO₂ systems were available, it seems unlikely that it will ever be possible to analyse in critical detail the factors involved in the consolidation of the dyke, the changes that are seen from interior to margin, and the evolution of the carbonated margin. However, the chemical data indicate that the process of marginal carbonation must have been significantly different from that of low-temperature hydrothermal metasomatism. The general absence of changes in the amounts of the analysed trace elements between the interior and margin of the dyke is regarded as significant in this respect. It is interesting to compare the composition of the carbonated Sròn Bheag rocks with that of a Carboniferous basalt, which has been subjected to the latter kind of alteration (MacDonald, 1973). This is similarly a pale cream-coloured rock containing about 8 % CO₂ and 3 % H₂O with siderite as the dominant carbonate, but it differs from the present example in containing an abundance of secondary quartz, and in the absence of sericite or any aluminosilicates, apart from albite.

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