Contrib Mineral Petrol (1985) 89:226–238

Contributions to Mineralogy and Petrology

The Criffell zoned pluton: correlated behaviour of rare earth element abundances with isotopic systems

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Abstract. Concentric zoning in the Criffell pluton takes the form of a discontinuous outer margin of metaluminous hornblende granodiorite and an inner core of increasingly peraluminous muscovite granite. Previous investigations using major and selected trace elements have shown the variation to consist of both smooth and abrupt trends. This study of 15 samples for the rare earth elements shows patterns which strongly correlate with Sr and O isotope data. The principal feature of these data is a progressive decrease in total rare earths with approach to the geochemical centre of the pluton, and evolution to more radiogenic Sr and more silicic and peraluminous compositions. No significant europium anomaly is developed. The slope of light to heavy rare earths using La/Yb ratios varies in a complex manner showing no significant correlation with any of the main indices of bulk composition, but with peak values occurring within the inner part of the outer portion of the pluton. A map of Ce/Y variation based on 172 Ce and Y determinations is essentially identical. These data are considered in terms of various petrogenetic models and it is concluded that the data can only be interpreted in terms of a major and progressive involvement of crustally-derived anatectic magma towards the pluton interior. Trace element modelling favours processes of the assimilation-fractional crystallisation (AFC) type for the generation of this example of I-type to S-type granitoid zonation.

Introduction

Concentric zoning of mesozonal plutons is a common phenomenon and compositional changes are frequently gradual without perceptible discontinuities. The trend of increasing acidity towards the core is normal for the majority of such plutons and the several processes which have been suggested to account for normal zoning were reviewed by Bateman and Chappell (1979). Field, petrographic, and whole-rock major oxide studies have largely been unsuccessful in quantifying the contributions that the various processes of fractional crystallisation, restite separation, contamination, and hybridisation make to the generation of a suite of chemically variable samples which usually display linear but scattered Harker and AFM trends, frequently interpreted as due solely to fractional crystallisation. Advances in the understanding of trace element behaviour in the melt-crystal environment have taken the form of mathematically defined processes which may be used quantitatively to test hypotheses of fractional crystallisation (see Allegre and Minster 1978 for review), of partial melting (Shaw 1977), of contamination by combined fractional crystallisation and wall-rock assimilation (DePaolo 1981), of mixing (Langmuir et al. 1978), and of cumulate formation (McCarthy and Groves 1979). These models may be used for modal or non-modal removal of crystalline phases from melt or residue (Hertogen and Gijbels 1976). The application of simple models to the petrogenesis of granitic rocks was recently reviewed by Hanson (1978). More complex models, probably more closely approximating the real physico-chemical situation, have been formulated which account for episodic histories, such as fractional crystallisation of a periodically replenished magma chamber (O'Hara et al. 1977). All models rely on a quantitative measure of the partition of the trace elements between each crystalline phase and the melt. Such partition coefficients have been obtained both experimentally and by analysis of phenocryst-matrix pairs, but for some elements show considerable T, fO_2, and melt composition dependence. In this study simple (i.e. modal crystallisation and non-replenished chamber) models only will be used to test conflicting petrogenetic hypotheses but with the introduction of the spatial dimension involved in normal zoning, and correlation with Sr and O isotopic data on the same samples. For the rare earth elements in granitoid matrices use will be made of appropriate experimental and phenocryst/matrix partition coefficients, choice being based mainly on the similarity of the matrix to the bulk composition of the granodiorite-granite series.

Normal compositional zoning in the Tuolumne Intrusive Series was recently investigated using rare earth elements (REE) by Frey et al. (1978). This pluton in the Sierra Nevada batholith has a slightly broader but similar compositional range to Criffell and also has a concentric pattern of zoning. The Tuolumne series ranges from quartz diorite at the margin to felsic granite porphyry in the core and has been interpreted as a comagmatic suite with crystal fractionation (particularly of amphibole) causing the compositional zonation. A detailed field and petrographic study of the Criffell granitoids and associated dykes led Phillips et al. (1981) to propose that the zoning was a function of separation and marginal accretion of early plagioclase, hornblende, biotite and magnetite crystals. Using bulk-rock major oxide data for 180 samples taken on a grid sampling pattern, Stephens and Halliday (1980) showed that the com-

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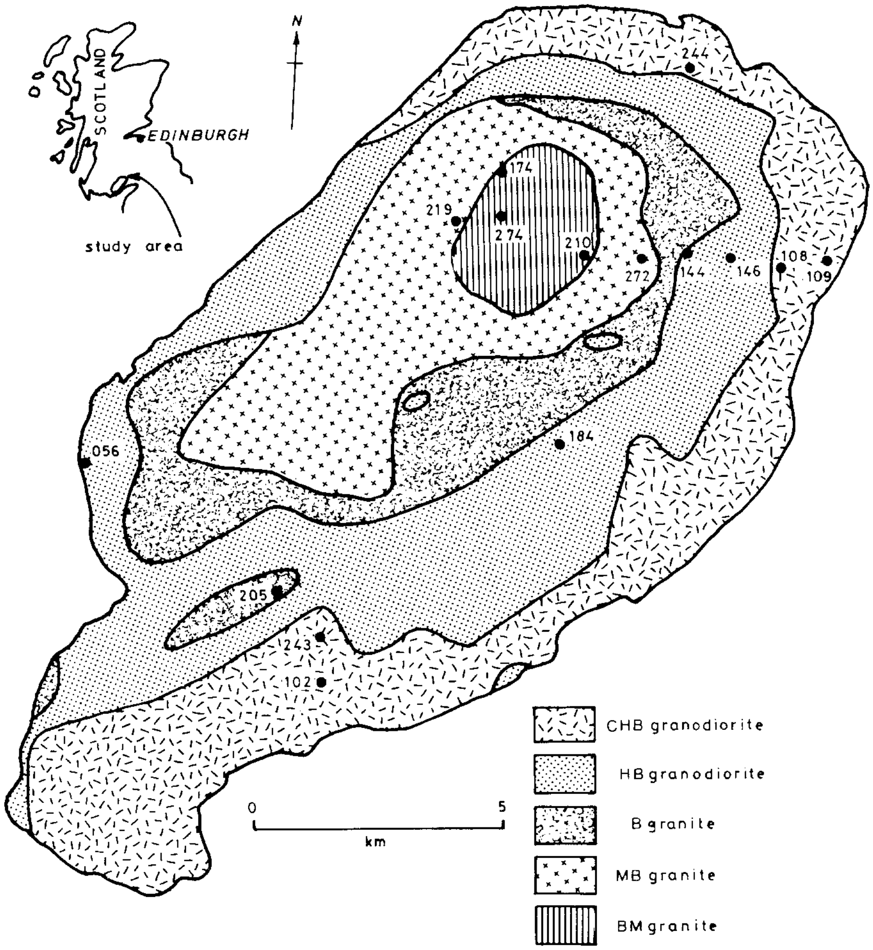

Fig. 1. Map of the petrological types in the Criffell pluton showing also the locations of samples used in this study. CHB refers to clinopyroxene (diopside) hornblende biotite granodiorites, HB are hornblende biotite granodiorites, B are biotite granites, MB are muscovite biotite granites, and BM are biotite muscovite granites

position surfaces for the pluton were far from regular and major compositional gradient variations showed there to be composite features superimposed upon normal zonation patterns. In addition the boundary zone between the outer granodiorite and inner granite represents a zone of partial equilibration between magma pulses. Halliday et al. (1980) interpreted variable Sr isotope initial ratios and $\delta^{18}O$ values as disclosing melts of different origins and the linear array of values on the $(^{87}Sr/^{86}Sr)_i$ versus $\delta^{18}O$ plot as being due to mixing processes, though the end-members were not constrained. They have argued in favour of a model with progressive incorporation of S-type melts into the core of the pluton.

The object of this contribution is to use REE distributions in a spatial sense to test between these models and to look for relationships between the REE patterns and the variable isotopic data in an attempt to understand better the processes involved in evolving concentrally zoned calcalkaline plutons and magma chambers. It will be shown that a simple inverse relationship exists between the absolute abundances of the rare earth elements and other compositional parameters, but ratios of light to heavy rare earths vary in a more complex manner which has an important bearing on the possible petrogenetic processes.

Zonation of the Criffell pluton

The pluton is early Devonian (397 ± 2 Ma, Halliday et al. 1980), post-tectonic, and intrusive into Silurian sediments of flysch facies. It was emplaced during or after closure of the Iapetus Ocean and the period 405 ± 15 Ma was a time of major igneous activity, particularly plutonic, on the northwestern continental margin of this ocean. The pluton is typically calcalkaline in chemistry and shows a range in SiO_2 values from 58% to 75%. It was probably emplaced at quite a high level in the crust as boulders of the granodiorite are found in arkoses of Lower Carboniferous age a few kilometres of the south.

The Criffell (Dalbeattie) pluton was first fully described by Phillips (1956) who presented a map of the distribution of petrologic types and described petrographic and structural aspects of the pluton. Essentially the zoned arrangement shown on a more detailed petrological map (Fig. 1) consists of an incomplete outer zone of clinopyroxene hornblende biotite (CHB) granodiorite, and hornblende biotite (HB) granodiorite which is often xenolithic and foliated. This surrounds an inner core of more isotropic biotite (B) granite, muscovite biotite (MB) granite, and biotite muscovite (BM) granite. No internal field contacts have been observed and Phillips (1956) argues that the granodiorite to granite change is of a gradual nature, without intrusive relationship. With the advantage of 180 samples collected on a grid over the whole pluton Stephens (in prep.) has reclassified the petrography and has divided the pluton into 5 petrographic zones, these being shown on Fig. 1 and used throughout this contribution. The recognition of two muscovite-bearing granite facies is an addition to the types previously described by Phillips (1956). Further textural studies have revealed a zone of porphyroclastic and mortar textures predominantly in the region of the boundary zone of Stephens and Halliday (1980) and may be attributed to late surging as postulated by Phillips et al. (1981). It is now clear from bulk geochemical work (Stephens and Halliday 1980) that a distinct compositional gap exists between outer and inner parts of the pluton and that the magnitude of this compositional step is variable. In the vicinity of the steepest chemical gradient a sharp field boundary between dark granodiorite and porphyritic granite can be traced to within 10 metres where HB granodiorite comes into contact with B granite between sample points 244 and 174 in the north of the pluton.

Stephens and Halliday (1980) made use of spatial analysis techniques to show that gradients in bulk composition vary considerably over the pluton. This was highlighted by using an approximation to the first derivative of the surface defined by fitting a grid mosaic of small planar surfaces derived by least squares polynomial regression, and calculating the maximum inclination of each plane. This first derivative was then itself mapped using values found by mapping the first derivative of SiO_2 [i.e. SiO_2'] in the same way as described in Stephens and Halliday (1980) and then interpolating back to the sample location.

Analytical methods

Samples of at least 1 kg were collected and fresh material was then crushed using a Sturtevant jaw crusher and Tema swing mill with tungsten carbide discs to 100 mesh. After homogenisation a further 50 g was crushed for 5 min in the Tema. XRF analysis for Ce and Y was performed on a Philips PW1212 and a Philips PW1400 using Ce Lα(1) and Y Kα radiation dispersed by LiF200 crystal. Mass absorption corrections were applied by calculation from the major element composition of the matrix. Precision estimates based on 20 of replicate analyses are 1 ppm for Y and 3 ppm for Ce.

The REE analyses presented in Table 1 were obtained by neutron activation analysis. Duplicate samples of 0.2 g were were irradiated for 6 h in a flux of 3.6×10^{12} n.cm^{-2} sec^{-1}. Gamma emitters with energies below 150 KeV were counted with a 0.5 cm planar Ge(Li) detector with a resolution of 623 eV at 122 KeV and gamma emitters with energies above 150 KeV were counted with an 80 cm coaxial Ge(Li) detector with a resolution of 2.2 KeV at 1.33 MeV. Both detectors were controlled by an EGG-ORTEC Data Acquisition and Analysis System which processed the resulting spectra to provide net photopeak areas for the isotopes of interest. Results were calculated by comparing the induced activites with those induced in samples of BCR-1 which were irradiated together with the samples of granite, and duplicates were found to agree within the errors imposed by the counting statistics. Such errors were normally better than +/− 2% for the light rare earths and +/− 5% for the heavy rare earths.

REE distributions

Chondrite-normalised plots are presented for all samples in Figs. 2a to e, using the 'best unfractionated' chondrite abundances of Evensen et al. (1978). The absolute rare earth abundances for the Criffell samples are presented in Table 1. A composite plot of the trends is shown in Fig. 2f. The five plots represent the five igneous facies of the pluton in evolutionary sequence (i.e. CHB, HB, B, MB, and BM). The composite plot (Fig. 2f) shows the sequence from clinopyroxene and amphibole-bearing granitoids to muscovite-bearing types to be one of total rare earth depletion. The CHB granodiorites of Criffell are the least evolved types and have the highest total REE, moderate La/Yb and no Eu anomaly (Table 2). Reference to the mean values for the petrologic types (Table 2) emphasises a general trend from the granodiorites with total (8) REE abundances in the range 140 to 200 through to muscovite bearing granites with the same totals ranging from about 50 to 120. Similarly, La/Yb values vary, but not as systematically. Some of the more evolved granodiorites and least evolved granites show the highest ratios of about 56, the lowest ratios of about 28 being in the most evolved muscovite granites. In this respect the areal distribution trend is interesting and will be discussed later. It is noted that no marked Eu anomaly is present, especially as plagioclase fractional crystallisation has been suggested as an important control (Phillips et al. 1981).

Petrogenesis

Variation from CHB granodiorites to BM granites is found within a range of 12% SiO_2, from about 61 to 73% (Ta-

Table 1. Rare earth element abundances and associated errors for samples from the Criffell pluton. Rock types as used in Fig. 1, Gd being granodiorite and Gr being granite. Average error is the mean of the 2σ errors determined from counting statistics

Sample no.	La	Ce	Nd	Sm	Eu	Tb	Yb	Lu	Rock type
056	38.3	72.0	28.8	6.15	1.07	0.28	0.90	0.11	HB Gd
102	51.1	87.8	28.6	5.33	1.55	0.50	1.17	0.18	CHB Gd
108	47.5	81.1	27.7	4.79	1.30	0.47	1.31	0.17	CHB Gd
109	50.3	94.4	35.5	6.08	1.56	0.47	1.39	0.27	CHB Gd
144	38.0	70.0	26.5	3.44	0.99	0.38	0.93	0.13	HB Gd
146	54.5	94.4	27.8	6.30	1.48	0.46	0.96	0.15	HB Gd
174	13.0	22.4	12.5	1.51	0.63	0.23	0.39	0.06	BM Gr
184	37.4	61.7	29.8	4.38	1.33	0.32	0.72	0.13	HB Gd
205	40.5	69.9	33.2	4.30	1.44	0.31	0.72	0.14	B Gr
210	22.8	53.9	18.3	3.17	0.73	0.31	0.80	0.11	BM Gr
219	26.4	51.5	21.5	4.46	0.82	0.33	0.81	0.12	MB Gr
243	52.9	88.5	29.2	5.28	1.00	0.39	1.22	0.17	CHB Gd
244	53.7	98.1	40.0	7.46	1.47	0.52	1.18	0.16	CHB Gd
272	31.3	56.5	22.4	4.46	0.84	0.30	0.82	0.14	MB Gr
274	23.4	45.3	18.7	4.41	0.76	0.30	0.86	0.11	BM Gr
Average error %	1.7	2.0	2.4	0.7	1.7	3.0	4.6	5.5	

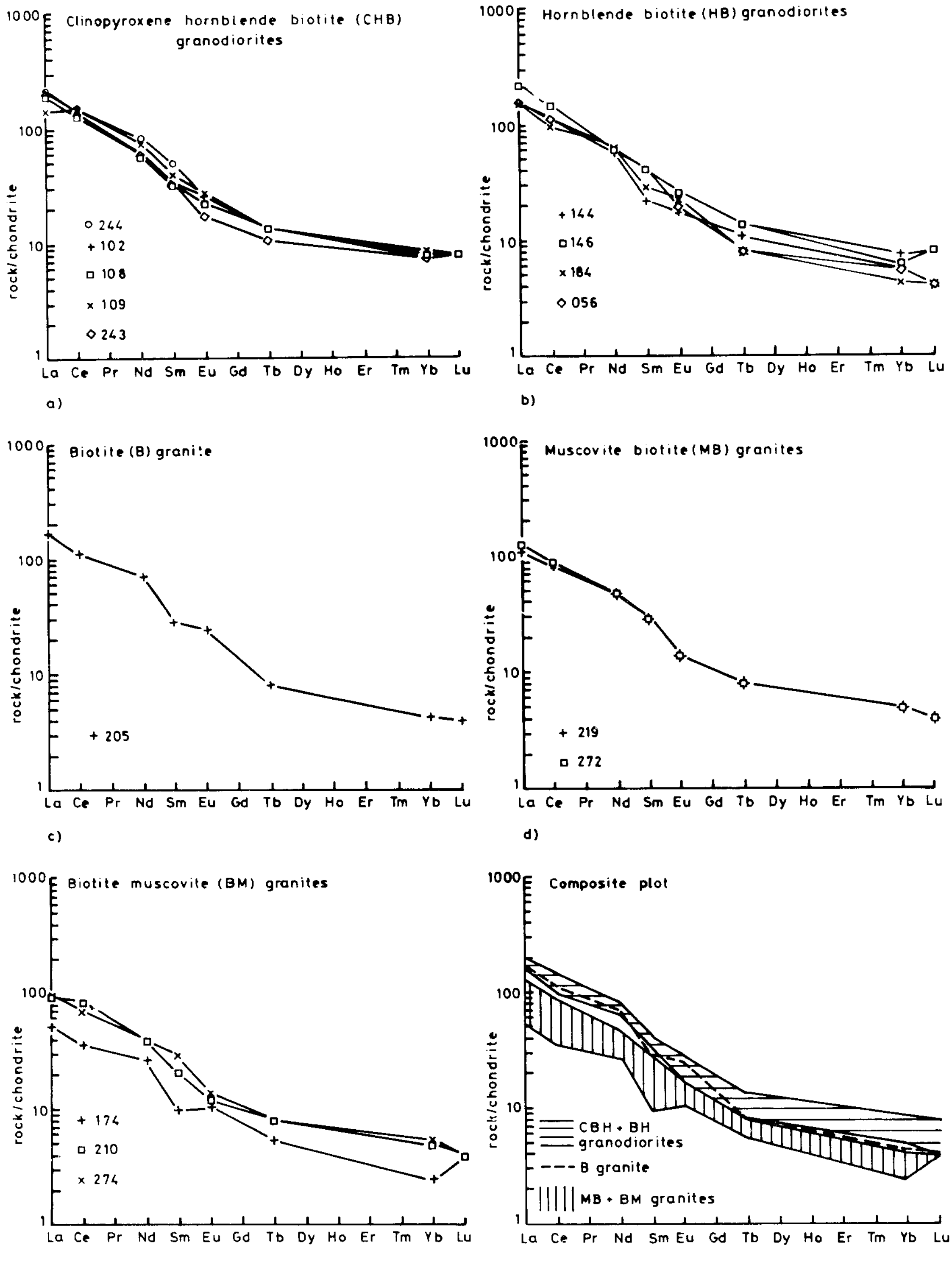

Fig. 2. a–e Chondrite normalised plots for 8 rare earth elements of each of the five petrological types in the Criffell pluton (see Fig. 1). Values are normalised to those of Evensen et al. (1978). **f** Composite plot showing fields for CHB and HB granodiorites, BM and MB granites. Single sample of B granite also shown

ble 2). Such variation may be accounted for by a variety of processes postulated at various times to account for bulk rock variations within silicic mama suites. Some "end-member" models are listed below.

a) Formation of marginal cumulates with subsequent removal of low density melt generating fractional crystallisation trends in the magma.

b) Magma intrusion as melt plus restite mush with magmas of the pluton interior being more restite-depleted than marginal magmas.

c) Composite intrusion of compositionally-distinct pulses with possible hybridisation.

d) Contamination of a single magma by assimilation of wall rocks.

Table 2. Selected composition parameters for the various petroloic types in the Criffell pluton. Sr and O isotope data taken from Halliday et al. (1980), Nd isotope data from Halliday (1984), and Nd isotope data for SULPS taken from O'Nions et al. (1983). SULPS = Southern Uplands Lower Palaeozoic sedimens, Gd = granodiorite, Gr = granite. Rock types accord with those on Fig. 1. Note that the Nd isotopic value for mean SULPS is not based on the same sample set as the other parameters for SULPS

Rock type	Sample	SiO_2	A/CNK	REE	La/Yb	Eu/Eu*	$(^{87}Sr/^{86}Sr)_i$	$\delta^{18}O$	εNd
CHB	102	63.08	0.92	176.2	43.7	0.97	0.70572		
	108	63.66	0.90	164.5	36.3	0.87	0.70545		
grano-	109	61.09	0.80	190.0	36.2	0.88	0.70533		
diorites	243	65.06	1.01	178.7	43.4	0.65	0.70563	9.05	−0.4
	244	64.35	0.94	202.6	45.5	0.69	0.70521	8.54	−0.6
HB	056	68.60	1.00	147.6	42.6	0.63	0.70602		
grano-	144	67.93	1.00	140.4	40.9	0.93	0.70602		
diorites	146	65.07	0.92	186.1	56.8	0.81	0.70541		
	184	67.91	1.08	135.8	51.9	1.05	0.70613		
B granite	205	68.68	1.09	150.5	56.3	1.16	0.70597		
MB	219	71.88	1.09	106.0	32.6	0.63	0.70734	11.89	
granites	272	70.32	1.09	116.8	38.2	0.66	0.70647		
BM	174	73.01	1.14	50.7	33.3	1.26	0.70688		
granites	210	71.98	1.12	100.1	28.5	0.76	0.70728		
	274	71.35	1.18	93.8	27.2	0.60	0.70602	11.77	−3.1
Mean SULPS		62.93	0.91				0.70755	12.49	(5.9)
Mean CHB Gd		63.45	0.91	182.4	41.0	0.81	0.70547	8.80	
Mean HB Gd		66.97	1.00	152.5	48.1	1.15	0.70596		
Mean B Gr		68.68	1.09	150.5	56.3	1.16	0.70597		
Mean MB Gr		71.10	1.09	111.4	35.4	0.65	0.70691	11.89	
Mean BM Gr		72.11	1.15	81.5	29.7	0.87	0.70673	11.77	

e) Soret-effect diffusion processes leading to compositional gradients within the melt.

f) Mass removal in a volatile phase.

These models and various realistic combinations of them will be discussed in terms of the constraints imposed by the rare earth data presented here and previously published isotopic data.

Constraints on petrogenesis

Before discussing the contributions of the above-listed "end-member" models to the petrogenesis of the Criffell pluton some of the constraints will be described.

Trend of decreasing REE abundances. This trend is abnormal, but not especially unusual in granite plutons, other examples from the Caledonian of Scotland being the Foyers and Strontian complexes (Pankhurst 1979). The sums of the 8 analysed REE have been mapped (Fig. 3a) and it is clear that the zonal distribution is emphasised by a 4-fold decrease in this parameter. It is noteworthy that the highest values occur in the northeast of the pluton and the most rapid fall-off in total-REE occurs in a traverse from this region in towards the BM granite. In the southwest the rate of change is much more gradual. Following the traverse from sample 109 to 174 (Fig. 1, Table 2) there appear to be two abrupt changes. Firstly, from 146 to 272 via 144, through the HB granodiorite to B granite into BM granite. Secondly, from 274 and 219 to 174, the latter being depleted in total-REE and is additionally most evolved in almost all other geological parameters. Ce and Y have been determined by XRF on a much greater number of samples (172) with a good geographic coverage (see Stephens and Halliday 1980 for locations). Maps of these are presented as being representative of light and heavy-like rare earths (Figs. 4a and b). Apart from a small region of high values >120 ppm the main feature of the Ce distribution is the general decrease towards values of 80 ppm in the granodiorites followed by a decrese from about 60 ppm to less than 40 ppm in the granites. Y shows much less regular patterns. The granodiorites are marked by very irregular Y values with maxima of about 18 ppm dropping to about 12 ppm. The granites also show irregular distributions of values of 10 ± 2 ppm except for the central BM granite where there is a marked depletion to a minimum of 4 ppm.

The following features are common to both total-REE on the limited number of samples and the 172 samples with Ce and Y determinations. (a) Irregular REE variations within the granodiorites; (b) the marked maximum within the granodiorites; (c) the significantly lower values in the granites; and (d) the sharp depletion in the BM granites, especially near sample 174. Petrogenetic models must explain these spatial features including the variations in rates of change in REE abundances over the whole pluton.

LREE/HREE. In view of the ability of amphiboles to fractionate HREE (Arth and Barker 1976) it is important to consider the variations of LREE/HREE over the pluton. Values for La/Yb are given in Table 2 and are mapped in Fig. 3b. These values range from 36 to 46 in CHB granodiorites, 40 to 57 in the HB granodiorites, 56 in the one B granite analysed, 33 to 38 in the MB granites, and 27 to 33 in the BM granite. There is a distinct trend of increasing La/Yb in the granodiorites towards the B granite, fol-

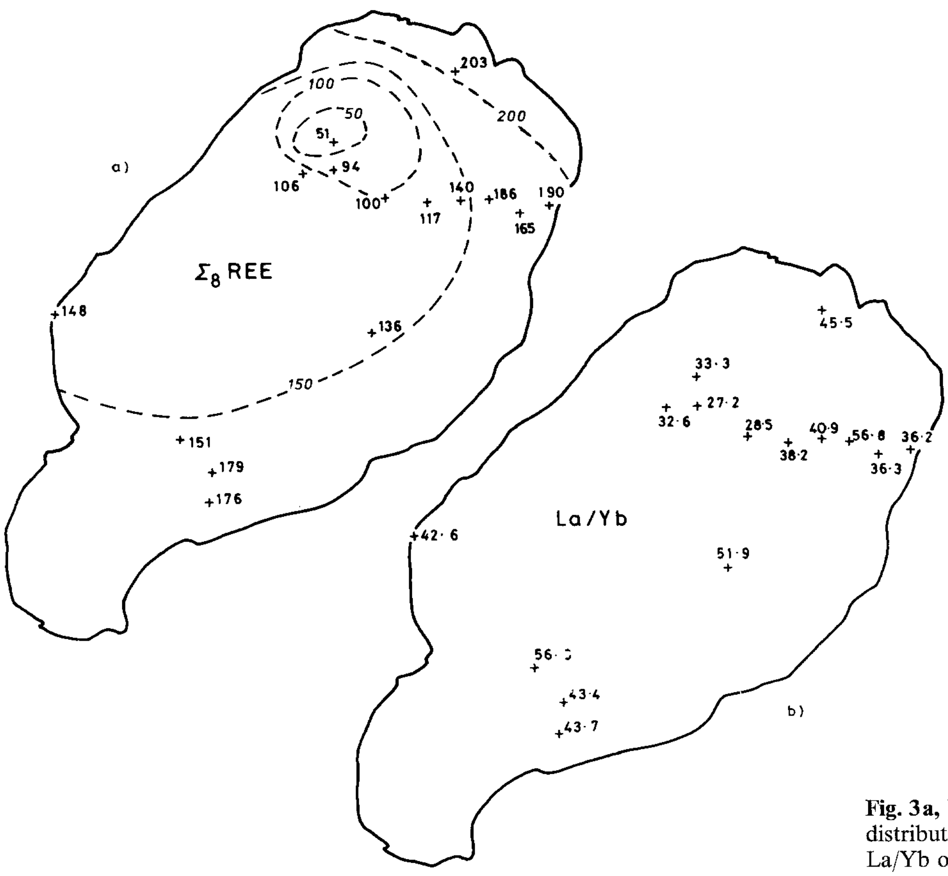

Fig. 3a, b. Maps of the distribution of total(8) REE and La/Yb over the Criffell pluton

lowed by a marked drop and continuing decrease in the muscovite- bearing granites (MB and BM granites). Taking the XRF Ce and Y data, a contour map of Ce/Y should reflect these LREE/HREE trends and this is shown in Fig. 4c where shaded areas represent Ce/Y ratios greater than 7. The internal ridge in values is almost continuous within the inner parts of the granodiorites and B granite, occasionally reaching as far as the outer contact. This figure shows values of Ce/Y greater than 7 and a ridge of these values is clearly persistent through the inner parts of the granodiorites and B granite.

This constrains petrogenetic models to explain the increase in granodiorite interior, and its subsequent decrease within the evolved granites.

Lack of Eu anomaly. Values of Eu/Eu* are presented in Table 2. These values do not represent significant anomalies. The granodiorites generally have small negative anomalies while the granites are variable but the most evolved biotite muscovite granite (174) has a significant positive anomaly. Most of these anomalies are small and few are beyond the limits pf error so the constraint imposed by this parameter is principally the lack of development of significant Eu anomalies, except perhaps for some of the evolved granites. This will certainly have a bearing on petrogenetic models involving plagioclase separation or accumulation. It should however be noted that biotite mineral separates from the granodiorites have high Fe^{3+}/Fe^{2+} ratios lying close to the magnetite-haematite buffer estimated by Wones and Eugster (1965) whereas the granite biotite separates have much lower fO_2 estimates scattered about the Ni−NiO buffer (Theofilopoulos, in prep.). Partitioning of Eu into plagioclase may not have been significant under the conditions of crystallisation of the granodiorite but would have been so when the granites crystallised showing an Eu anomaly if plagioclase had been removed or accumulated (assuming that it would not be masked by complementary behaviour in other minerals). This is interpreted to mean that the Eu anomaly values do not constrain plagioclase behaviour in the granodiorites but do suggest minor plagioclase removal prior to consolidation of the granite magma.

Correlation with other parameters. Five parameters have been selected as measures of different aspects of the various rock compositions. *SiO_2* is an index of the bulk major oxide composition. *A/CNK* (molar $Al_2O_3/[CaO+Na_2O+K_2O]$) reflects the abundance of Al_2O_3 relative to that required to make feldspars from all the Ca, Na, and K, values of >1.0 being peraluminous. *Total REE* is a reflection essentially of the light REE, especially La and Ce. $(^{87}Sr/^{86}Sr)_{397}$, the initial Sr isotope ratio at 397 Ma, should be independent of degree of fractional crystallisation alone. $\delta^{18}O$ is slightly affected by fractional crystallisation but is very sensitive to source composition (O'Neill and Chappell 1977). This has been determined on four samples only. The parameters selected encompass major and trace elements, radiogenic and stable isotopes, and are variously sensitive to the processes to be discussed. Significant linear correlations exist for all 10 combinations of these parameters and the plots are presented in Fig. 5. It is clear from these plots that the marked positive covariation between SiO_2, A/CNK and the isotopes, and the marked negative covariation between these and the total REE imposes additional con-

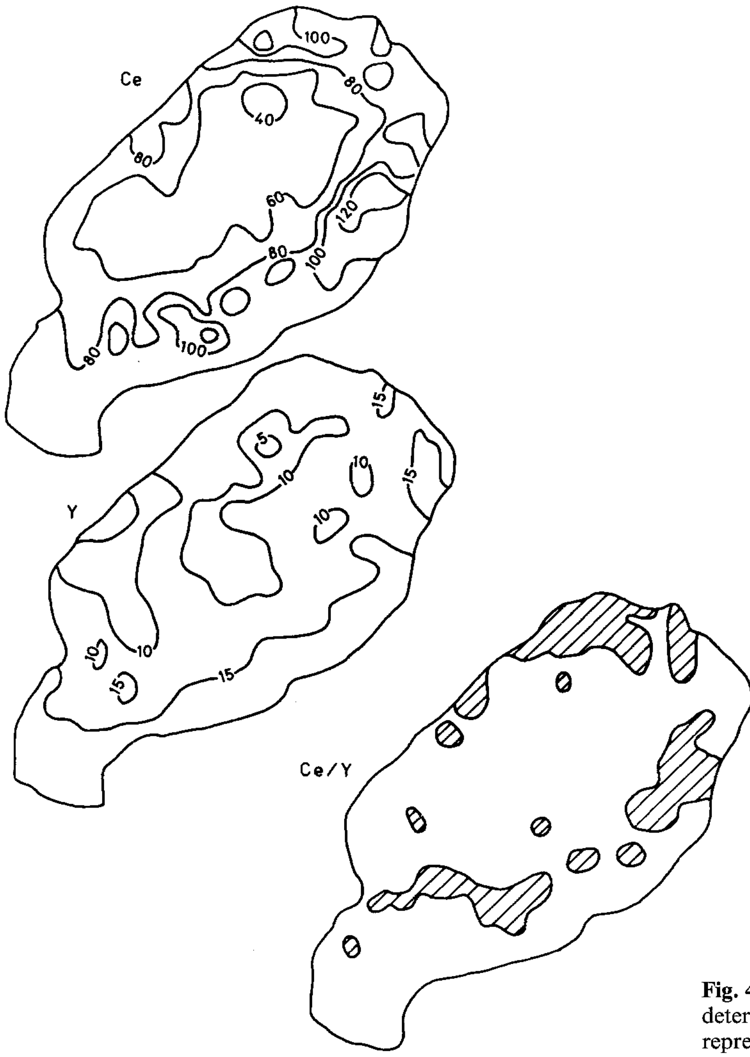

Fig. 4. Maps of Ce and Y abundances and Ce/Y determined by XRF on 172 grid samples. Shaded area represents values where Ce/Y is greater than 7

straints on petrogenesis. Thus petrogenetic models must explain progressive evolution in bulk rock composition and Sr and O isotopes towards more acid, peraluminous, and isotopically enriched values while depleting the total rare earths.

Fractional crystallisation

In modal terms the granodiorite to granite trend is one of the removal of diopside, amphibole, andesitic plagioclase and sphene and the replacement of these by a more sodic plagioclase, more quartz and K-feldspar. The occurrence of primary muscovite in the granite is a further evolution within the granites. Removal of a calcic plagioclase and amphibole (plus minor clinopyroxene) as near-liquidus phases would have the desired effect of increasing the SiO_2 concentration and if the amphibole is sufficiently Al-deficient then peraluminous compositions would occur at higher SiO_2 levels. It is generally acknowledged that common calcic amphiboles will partition heavy REE (Arth and Barker 1976) and could give rise to the increased LREE/HREE observed within the granodiorite.

It is likely that REE are distributed dominantly amongst accessory minerals such as sphene, apatite and zircon which are common in this pluton. Sphene is especially abundant in the granodiorite. A study of a granodiorite from the eastern Peninsular Ranges batholith, Southern California by Gromet and Silver (1983) has shown that from 80 to 95% of each rare earth element is to be found within sphene and allanite. Thus the ability of these minerals to control rare earth patterns during fractional crystallisation must be recognised. The decreasing total rare earths of the Criffell pluton may well be explained by removal of small amounts of such accessories. Modal abundances of accessories in a basic granodiorite (109) are sphene 1.9%, apatite 0.4% and zircon 0.4%. Sphene forms large euhedral crystals (often up to 2 mm) and must be an early liquidus phase which completed crystallisation before the bulk of the remaining phases as impingement textures are rare. Similarly apatite is commonly euhedral and forms small crystals scattered throughout mafic phases and the groundmass of the granodiorite. Depletion within the granodiorite of all the rare earths may be due largely to the removal of sphene and possibly apatite. However, the increasing ratios of LREE/HREE within the granodiorite may indicate the removal of hornblende, or alternatively the accumulation of hornblende in the outer granodiorites.

Whichever mineral fractionation scheme is preferred, none satisfies the constraints imposed by the isotope systematics. The shifts of about 0.002 in $(^{87}Sr/^{86}Sr)_i$ and 3.4 per mil in $\delta^{18}O$ cannot be accounted for by such schemes. Lee et al. (1982) found shifts of about 2 per mil in the

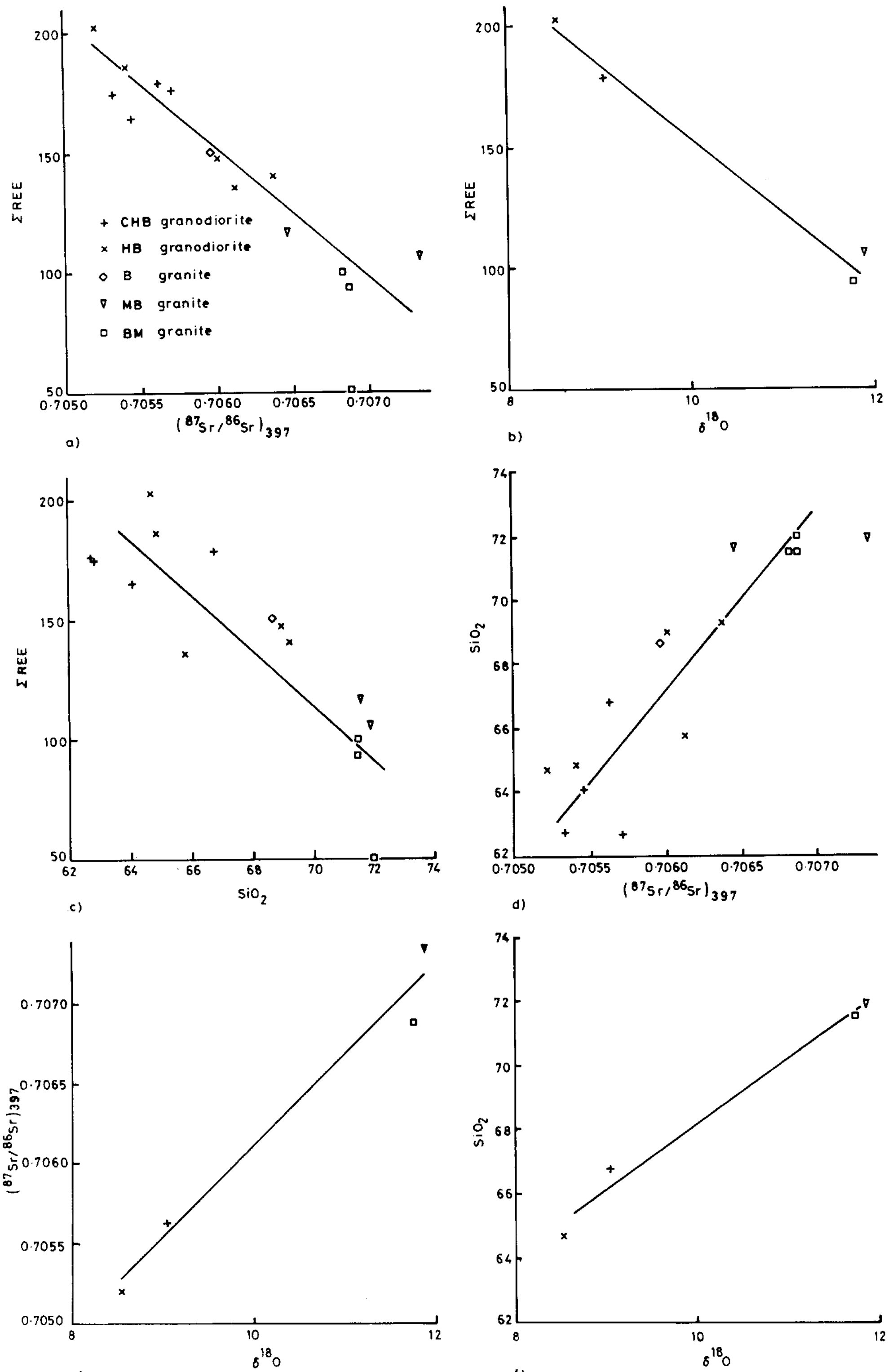

Fig. 5. Bivariate plots of all combinations of total(8) REE, $(^{87}Sr/^{86}Sr)_i$, $\delta^{18}O$, SiO_2, and A/CNK

Snake Creek-Williams Canyon intrusive and after analysing the oxygen isotope abundances of individual mineral phases ascribed the whole-rock variation to 'unusual concentration of ^{18}O-poor minerals in the mafic part of this intrusive'. A more normal limit to $\delta^{18}O$ enrichment during fractional crystallisation would be less than 1 per mil (Taylor and Silver 1978). Again Muehlenbach and Byerly (1982) have shown a shift of 1.3 per mil within a basaltic suite to require 90% fractionation. The considerable increase in $(^{87}Sr/^{86}Sr)_i$ in the felsic members of the pluton would require consider-

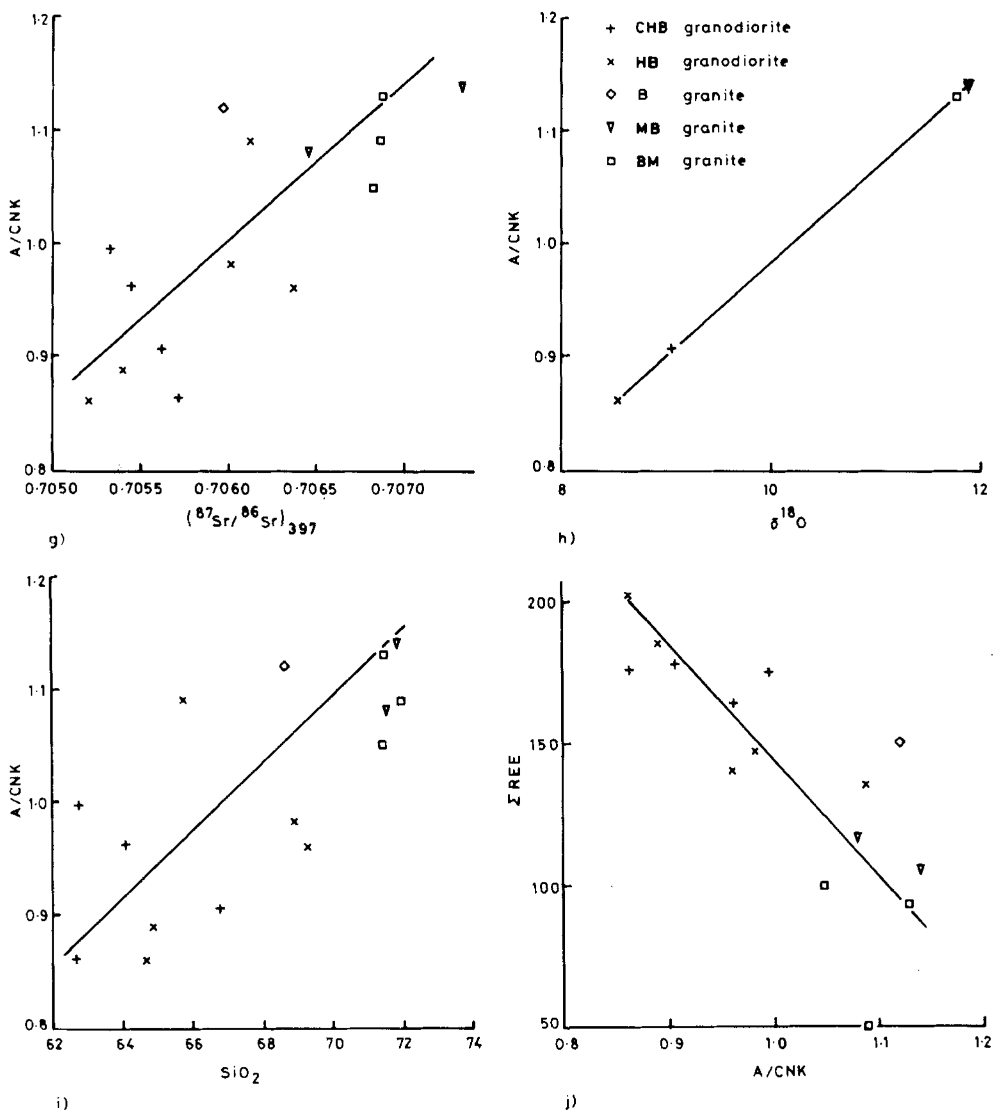

Fig. 5

able concentration of Rb in the late melt, or alternatively a considerable period of time. Taking the most favourable Rb/Sr value, 1.7, simple model calculations indicate a period of 31 Ma to develop the observed range in initial ratios.

It is concluded that fractional crystallisation alone could account for the rare earth distribution patterns by removal of sphene-dominated accessory phases along with amphibole and plagioclase, however this process will not satisfy the constraints of the correlating stable and radiogenic isotopes.

Cumulate formation

Trace element distribution patterns for cumulates will differ significantly from those of fractionally crystallising magmas as shown by McCarthy and Hasty (1976). However, this process also fails to satisfy the isotopic constraints described above. Although the marginal granodiorites with their mafic rich character may be good candidates for cumulates, cumulate-formation cannot be the principal petrogenetic process in this pluton.

Restite separation

The progressive unmixing of solid restitic material from granitic magma has been suggested as a means of generating normally zoned plutons (White and Chappell 1977). Texturally, many features of the outer granodiorite of Criffell could be interpreted as I-type restite. It is a xenolith-rich rock with abundant glomeroporphyritic amphiboles, diopside-cored amphiboles, and subhedral magmatic amphiboles. Plagioclases commonly show overgrown resorbed features. Mafic clots are abundant. Purging of this material would certainly give rise to many of the observed chemical trends, but again the isotopic constraint is not satisfied. This assumes that restite and melt are in isotopic equilibrium, and a study of xenoliths from the outer part of the granite indicates that this was the case (Halliday et al. 1980). The increase in La/Yb (Fig. 3b) and Ce/Y (Fig. 4c) in the inner part of the granodiorite and the biotite granite could be explained by removal of restitic amphibole extracting HREE and Y relative to the LREE. Field and petrographic evidence favour restite separation as a process, but it is probably of second-order importance in this pluton.

Composite intrusion

A distinct chemical break occurs within the pluton (Stephens and Halliday 1980) and this occurs in the vicinity of the HB granodiorite-B granite boundary. The magnitude of this break is variable, there being a chemical hiatus in all variables of varying magnitude along the boundary. The rocks on either side of the break may be considered to be products of distinct magmatic pulses, the outer granodiorite being essentially I-type, the inner granite having some characteristics of S-types but not strongly so. The fact that isotopic characteristics (Halliday et al. 1980) and rare earths show continuous variations suggests that if two such pulses existed as distinct entities then they have produced a series of intermediate hybrids which occupy intermediate regions within the pluton. The end-members would have approximately the following characteristics: Granodiorite end-member SiO_2 62%, A/CNK 0.85, $(^{87}Sr/^{86}Sr)_i$ 0.7050, $\delta^{18}O$ 8, Ce 100 ppm, Y 16 ppm. Granite end-member SiO_2 73%, A/CNK 1.20, $(^{87}Sr/^{86}Sr)_i$ 0.7075, $\delta^{18}O$ 12, Ce 20 ppm, Y 4 ppm.

These parameters for other samples would be expected to fall on mixing lines between these end-members and the data are largely consistent with this interpretation. Halliday (1984) has shown a shift in εNd from -0.4 in granodiorite 243 to -3.1 in granite 274 which suggests the involvement of a metasedimentary-contaminated magma for the central granite.

The implications of this conclusion are that the later granite pulse was of a rare earth depleted magma. This is likely to be the case if garnet and accessory allanite (or, to a lesser extent zircon or monazite) are restitic. High melt Fe/(Fe+Mg) values at high pressures favour restitic garnet (Clemens and Wall 1981). Plutons with marked REE depletions are known, eg. those of the Ruby Mountains, Nevada, USA. These are markedly peraluminous being garnet and two-mica bearing and have been ascribed by Kistler et al. (1981) to an S-type source.

Contamination by assimilation of wall rocks

Simple assimilation of wall-rocks is not likely to have occurred extensively in this pluton, the abundant xenoliths are amphibolitic or dioritic and are of cognate or exotic origin. No evidence for assimilation on any scale has been found and the study of Halliday et al. (1980) indicates that the local Silurian country rocks of flysch type would have had strontium isotopic ratios of greater than 0.71, whereas marginal types have the lowest initial ratios. Thus marginal assimilation must be rejected. Contamination through the roof providing material for the core of the pluton is an alternative but must account for the gradational nature of the compositional variation. Metasedimentary xenoliths in any state of assimilation are virtually confined to the outer 0.5 km of the pluton and there is a virtual complete absence of xenoliths of any kind in the pluton interior. This field evidence suggests that process is not important. The energy required to melt rocks which have never been heated above prehnite-pumpellyite facies temperatures (Oliver and Leggett 1980) would also seem to diminish the importance of this process.

Thermogravitational diffusion

This process, combining the effects of convective circulation and Soret diffusion can give rise to chemical gradients within melts. It has been applied to rhyolites (Hildreth 1981) and granites (Whalen 1983) but appears to be applicable to high silica compositions (75–77% SiO_2) only. The Bishop Tuff example shows marked LREE enrichment with SiO_2 increase, but the Ackley City granite example shows LREE depletion. Presently, without the benefit of trace element distribution models, it is difficult to test whether this process could have been involved in the generation of the compositional variation at Criffell (>10% SiO_2), but it seems unlikely to be capable of generating the observed isotopic variations.

Volatile mass transfer

Mass transfer in a vapour phase of required constituents was proposed by Vance (1961) to explain the evolved compositions in the interiors of many zoned plutons. Alternatively, the interior may have lost volatiles out of the system taking alkalis to drive the pluton to peraluminous compositions. This process is favoured by Goad and Cerny (1981) for peraluminous granites in Manitoba, and by Muecke and Clarke (1981) for the South Mountain Batholith in Nova Scotia. It is difficult to envisage how these processes would substantially but regularly bring about increase in Sr initial ratio. Little evidence for vapour saturation can be seen in the Criffell pluton, no miarolitic cavities and very few pegmatites, and the regularity of the observed variations does not favour this process. Although, again, this process may have contributed to the overall variation patterns, presently its quantitative contribution is not known but is suspected to be trivial at the early stages and small at the end.

Complex models

The combinations of some of the above processes can lead to models which can account for most and even all of the petrogenetic constraints described above. Satisfying the isotopic constraint seems to require the involvement of at least two magma sources, whereas the continuous nature of the variations could be explained by end-member mixing but not by fractional crystallisation alone. The recent modelling of combined assimilation and fractional crystallisation (AFC) by Allegre and Minster (1978) and DePaolo (1981) has been used as a test of this process for the Criffell zoned pluton.

AFC modelling. Assimilation of wall-rocks accompanying crystallisation is a process that has long been recognised (Bowen 1928). The only exposed wall-rocks in the Criffell region are the Southern Uplands Lower Paleozoic sediments (SULPS). For modelling purposes sediment (mean SULPS) compositions have been taken from the data of Halliday et al. (1980) and new data (Table 2). Model parameters are as follows:

Granodiorite end-member, sample number 244, Ce 98 ppm, Y 15 ppm, Ce/Y 6.53, $(^{87}Sr/^{86}Sr)_i$ 0.70521

Metasedimentary end-member, mean SULPS, Ce 55, Y 25, Ce/Y 2.20, $(^{87}Sr/^{86}Sr)_i$ 0.70755

During fractional crystallisation minerals are removed modally in the proportions plagioclase 66, amphibole 33, sphene 1.5, apatite 0.5, and zircon 0.5. These proportions are representative of modal mineral abundances in cognate dioritic clots within the granodiorites. In the AFC model a value of 0.3 is taken for Ma/Mc, i.e. the ratio of the

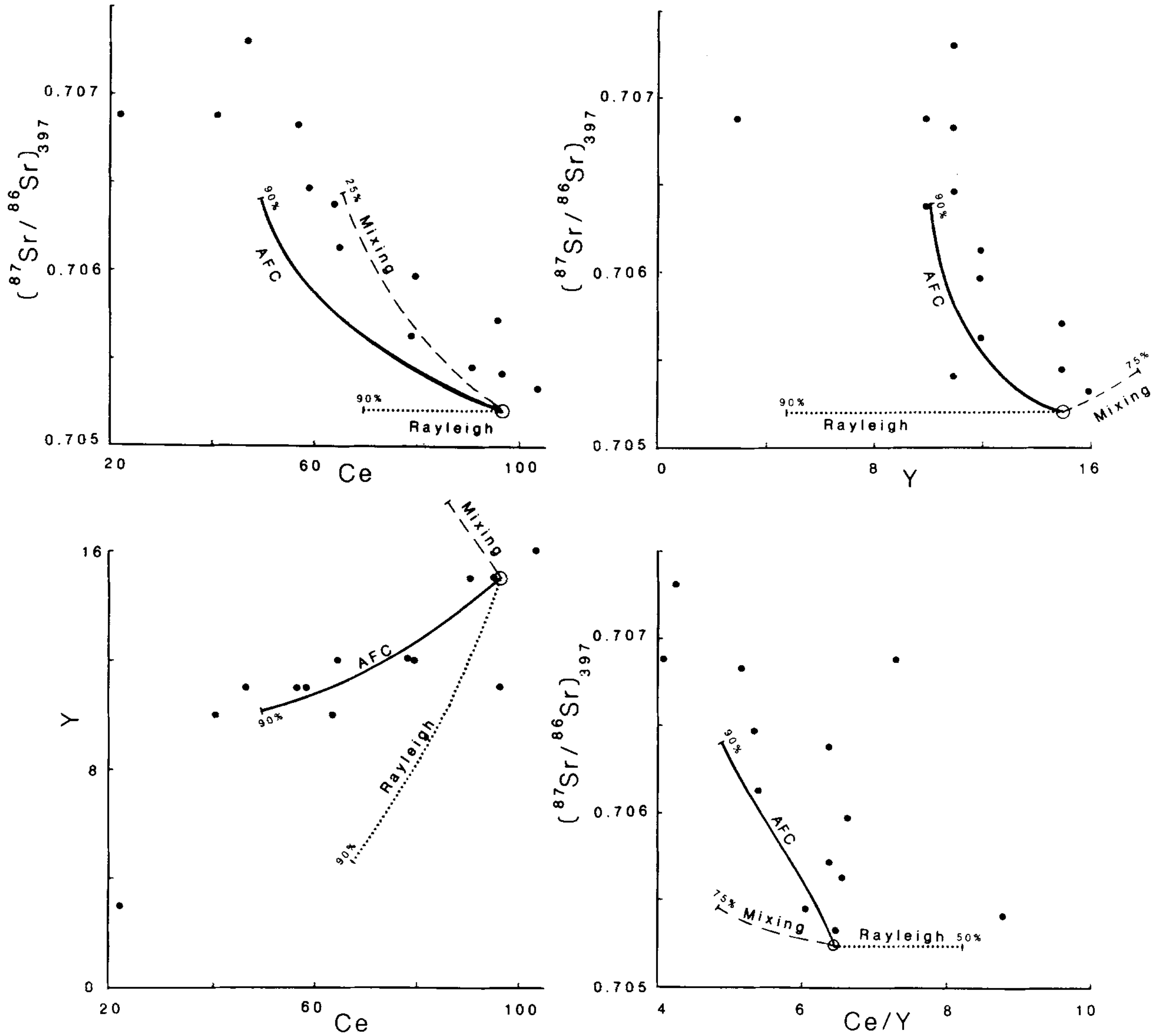

Fig. 6. Model trends for AFC, Rayleigh fractionation and mixing for various combinations of Ce, Y, Ce/Y, and $(^{87}Sr/^{86}Sr)_i$. End-members compositions and model assumptions described in the text. Partition coefficients are derived from Hanson (1978), Arth and Barker (1976), Nicholls and Harris (1980), Watson and Capobianco (1981), Drake and Weill (1975), Nagasawa (1970), Nagasawa and Schmetzler (1971), Schnetzler and Philpotts (1970), and Higuchi and Nagasawa (1969) selecting closest approximations to granodiorite compositions for appropriate minerals. In the case of apatite some interpolation of figures has been made where partition coefficients are unavailable

mass assimilated to the mass crystallised. Results are compared results for three types of model, namely (1) simple Rayleigh Law fractional crystallisation, (2) simple two end-member mixing, and (3) AFC processes (Fig. 6). Comparing all combinations of Sr isotope initial ratio, Ce, and Y, if is clear that the chosen AFC model conditions are overall a better fit than either simple mixing or Rayleigh fractionation. As many assumptions go into the AFC model and the sedimentary end-member is poorly constrained, the model should not be regarded as representing any precision. However, the model is capable of reproducing the REE-Sr isotope trends of the observed data unlike any other process. This model predicts that the evolved granites will be generated after about 90% crystallisation of the magma and this would appear to be of the right order for the relative volumetric relations.

The precise mechanism of AFC in zoned pluton generation cannot be determined from these data. Given the spatial relationships of the pluton it would seem that the process gives rise to evolved acidic magma compositions, and it is possible that these derived compositions have such high viscosities and high yield stress Bingham body characteristics that the spatial zonation is a function of delay in magma escape rather than any high-level process. Alternatively, the abundance of xenoliths in the granodiorite and the paucity of xenoliths in the granite may indicate that the degree of assimilation within the granite was greater, it being hotter for longer. However, the overwhelming majority of xenoliths in the granodiorite is of dioritic type and not metasedimentary (Holden, pers. comm.) and not potential end-members for the AFC processes described here. High LREE/HREE values within the pluton (Figs. 3b and 4c) may reflect the domination of amphibole and accessory mineral removal to be followed by contaminated magma which did not crystallise amphibole and was depleted in accessory phases. This later magma appears to have undergone some fractional crystallisation as proposed by Halliday et al. (1980) but this probably involved phases which did not significantly modify the REE abundances.

Composite intrusion, fractional crystallisation and hybridisation

The alternative model of deriving the magmas from distinct pulses, typified by samples 244 and 174 does not preclude the operation of fractional crystallisation processes within pulses or hybridisation between pulses, and the former has been discussed above. The latter process of hybridisation between pulses was appealed to by Stephens and Halliday (1980) to explain the variation in the compositional gradients at the boundary zone between pulses. The high-level compositional patterns may also reflect differential rates of AFC processes at depth generating differential compositional gradients on emplacement without prior homogenisation. It is difficult to test between the AFC model described above and model of partial hybridisation of two distinct pulses with some superimposed fractional crystallisation, the difference being the former involves contamination by solids the latter contamination by melt. At depths where metasediments might easily melt, the processes might be considered variants of the same contamination process.

Conclusion

AFC modelling of the isotopic and REE abundances in the Criffell zoned pluton fits the observations well. The data are consistent with a contaminant being local metasedimentary rock of Lower Palaeozoic age. The parental magma was an I-type crustally-derived magma of granodiorite composition. The contamination probably took place in the middle crust near the base of the accretionary prism of flysch sediments. Processes of the AFC type may be very important for the generation of plutons which zone from early I-type to later S-type compositions.

Acknowledgements. WES is indebted to Dr. W.J. Phillips for introducing him to the Criffell pluton and the fascinating problems it presents, and for many discussions on the origin of zoning. Alastair Moyes kindly read an early draft of the manuscript and made helpful and constructive comments. We would also like to thank Professors E.K. Walton and H. Wilson for providing facilities for completing thus study. George and Juliet MacQueen provided cheerful logistic support to field work and A. Wilson assisted with the neutron activation analysis. Richard Batchelor and Alastair Reid helped with XRF analysis.

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Received July 13, 1982; Accepted October 30, 1984