Secondary elemental mobility within the Støren greenstones, Norway

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A treatment of the geochemistry of both pillowed and massive lavas from the Benna area, Trondheim, is presented. Normally 'immobile' elements (TiO_2, Hf, Sc, P_2O_5 and REE) are shown to have been susceptible to very significant degrees of post-crystallization mobility. The pillow lavas are relatively depleted in these elements compared to the less altered massive lavas, while the three components of individual pillows have systematic differences in chemistry and elemental ratios. In particular, rare earth element (REE) rich components (pillow selvedges) have higher light rare earth element (LREE)/heavy rare earth element (HREE) ratios. During these secondary geochemical changes, trace elements and REE behaved coherently as indicated by the presence of strong interelement correlations. As the degree of carbonatization can be clearly related to the concentration of these elements, carbonate rich domains being relatively depleted in comparison to carbonate poor domains, the redistribution of chemistry is attributed to metasomatism involving a CO_2 rich fluid phase. This condition would enhance the mobility of these high valency cations by the formation of carbonate complexes. As this metasomatic process can be modelled using the Rayleigh distillation law, and because fractional crystallization is subject to the same law, caution is advised in the use of trace elements and REE in constructing petrological models for metamorphosed basic sequences. In addition, it is shown that the probable primary igneous composition of these greenstones is not unique to any specific geotectonic environment.

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This paper presents a treatment of geochemical data previously published by Loeschke (1976) and Loeschke & Schock (1980). The main purpose is to show that significant and systematic differentiation between light, medium and heavy rare earth elements has occurred in some of the Norwegian Støren greenstones, a feature not discussed by Loeschke & Schock (1980).

The Støren greenstones are an extensive succession of Cambro-Ordovician metabasalts occurring south of Trondheim, Central Norway. Recently their origin has been in dispute, with Loeschke & Schock (1980) advocating probable island arc affinities and Furnes & Roberts (1980) interpreting their geochemical data as being more indicative of ocean-floor basalts. Roberts, however, did mention that ongoing geochemical work suggests that the younger lavas of the Støren group approach basalts of within-plate character. The present note, although not strictly dealing with the geochemistry of these greenstones in relation to possible geotectonic environments, accepts Robert's opinion that primary stratigraphic variations in the basalt geochemistry of the Støren group are possible, and therefore discusses lava flows from one locality alone.

Most of the basic volcanics (exceptions N60-N64, N121-N123b, N112) analysed by Loeschke (1976) and Loeschke & Schock (1980) are from the Bymark greenstones (Carstens 1960). These rocks lie to the norht of the Horg syncline in Sør Trøndelag while the Støren greenstones (senso stricto) are on the southern limit. Although often considered the same, and collectively known as the Støren greenstones, or Støren group, their relationship has not been firmly established (Furnes et al. 1980). The volcanics discussed here are from the Benna area, 30 kilometres south of Trondheim. Although these have been described in some detail by Loeschke (1976) and Loeschke & Schock (1980), a brief summary of their findings is presented here for ease of reference.

These lavas are only slightly deformed and have been metamorphosed to between prehnite-pumpellyite facies and lower greenschist facies. Pillow lavas, with pillows showing primary shapes, form layers separated by massive lavas which constitute thicker flow units. Individual pillows are zoned with a dense green core, a light green epidote rich inner rim containing many round, elliptic or irregular patches and an outer dark green chlorite-rich selvedge. The selvedge represents the original glassy rim of each pillow.

A chlorite matrix occurs between separate pillows and is probably the alteration product of glassy hyaloclastite material (Loeschke 1976).

There are marked mineralogical differences between the three pillow components. The pillow cores comprise a fine-grained intergrowth of actinolite, epidote, chlorite, feldspar, quartz, carbonate and leucoxene. Occasional varioles and pseudomorphs of carbonate, chlorite, epidote (and quartz) after pyroxene (or feldspar) are present (Loeschke 1976), while chlorite, epidote and carbonate are alteration products of the original glassy interstices. Chlorite, carbonate, pyrite and leucoxene filled amygdules also occur.

The inner rim is epidote rich and strongly variolitic. Within the inner part of this component varioles usually impinge on each other, but outwards they are separated by a fine-grained intergrowth of chlorite and actinolite. The pillow selvedges comprise aggregates of fine-grained chlorite and actinolite. Epidote is rare while leucoxene is enriched, particularly around varioles and colloform textures. The interpillow matrix is mineralogically similar to the pillow selvedges.

The massive lavas, although coarser grained, have similar mineralogies to the pillow cores, with the addition of stilpnomelane, barroisitic hornblende and occasional biotite.

Loeschke (1976) has shown that the major element variations with the Støren volcanics have been produced by submarine devitrification and low grade metamorphism. Normative orthopyroxene, cordierite, spinel and corundum recorded for many of the samples provide a strong indication of the intervention of secondary processes. Further evidence for post-crystallization alteration is the presence of a well-developed "metamorphic differentiation" trend when D.I. (differentiation index) is plotted against certain major elements (SiO_2 and MgO). A measure of the secondary mobility is that within individual pillows TiO_2 is enriched within the selvedges. As the selvedges represent the chilled margins of a pillow, in common with recent observations from modern basalts (Moore 1965) their chemistry should be representative of the pillow as a whole. As this is clearly not the case within these volcanics, Loeschke (1976) concluded that TiO_2, normally considered to be very immobile during secondary alteration, can be susceptible to post-crystallization chemical changes.

Subsequent research into the REE geochemistry of these volcanics (Loeschke & Schock 1980) has revealed that REE must be sensitive to late alteration processes as they are preferentially enriched in the pillow selvedges. This redistribution was interpreted to have taken place within the glassy parts of pillows during submarine weathering and metamorphism. Loeschke & Schock (1980) suggested that the incompatible (an element with a greater affinity for the residual liquid rather than crystallizing phases) nature of REE during crystallization of the core would produce REE-enriched glasses within this part of the pillow compared to those of the rapidly chilled less crystalline selvedges. Thus if REE migration was restricted to the easily altered glasses, REE enrichment of the selvedges would result. An important conclusion of their work is that the less altered massive lavas, which are relatively enriched in REE, are probably closer to the initial igneous composition than the more altered pillow lavas, which are more depleted in REE.

Major element geochemistry

The complexity of secondary major elements redistribution in basic volcanic sequences has been documented by many authors (Scott 1976, Philpotts et al. 1969, Smith 1968). As the behaviour of major elements is very dependent on the conditions of alteration and metamorphism, and because these conditions are highly variable, a variety of major element redistribution patterns may be produced. Thus, a given element may be lost in one environment (with certain alteration conditions) but enriched in another. In fact, a lack of geochemical trends within altered basic volcanic sequences, is often considered a good indication of post-crystallization chemical mobility. The main problem arising from this is the identification of primary igneous compositions and trends. These are frequently masked or, in extreme cases, totally obliterated. A further problem, as outlined by recent workers, is that metasomatism and the late redistribution of major elements can produce geochemical variations analogous to primary igneous trends (Hellman et al. 1979, Donnelly et al. 1980). The discussion that follows focusses on the geochemical features of the Benna volcanics which may be of primary or secondary origin and attempts to decide which process is the more likely.

Although Loeschke (1976) has already outlined many of the geochemical characteristics of the Støren volcanics, analysis of his geochemical data by the present author has revealed some

Table 1.   Correlation coefficients for major elements from 10 massive lavas and 4 pillow cores of the Benna greenstones.

|	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	H_2O	P_2O_5	CO_2
SiO_2													
TiO_2	-0.064												
Al_2O_3	-0.244	0.159											
Fe_2O_3	-0.083	0.536	0.012										
FeO	0.106	0.882	-0.096	0.427									
MnO	-0.333	0.785	-0.363	0.444	0.844								
MgO	-0.245	-0.147	0.679	-0.042	0.475	0.102							
CaO	0.017	-0.666	-0.334	-0.440	-0.700	-0.501	-0.496						
Na_2O	0.203	0.272	0.207	-0.181	0.761	-0.016	0.134	-0.543					
K_2O	-0.012	0.807	-0.429	0.677	0.615	0.315	-0.444	-0.307	0.058				
H_2O	-0.409	0.368	0.384	-0.455	0.621	0.482	0.662	-0.788	0.259	0.048			
P_2O_5	-0.154	0.961	-0.399	0.645	0.841	0.800	-0.260	-0.546	0.170	0.900	-0.109		
CO_2	0.059	-0.488	-0.473	-0.490	-0.772	-0.476	-0.703	0.911	-0.358	-0.108	-0.765	0.364	
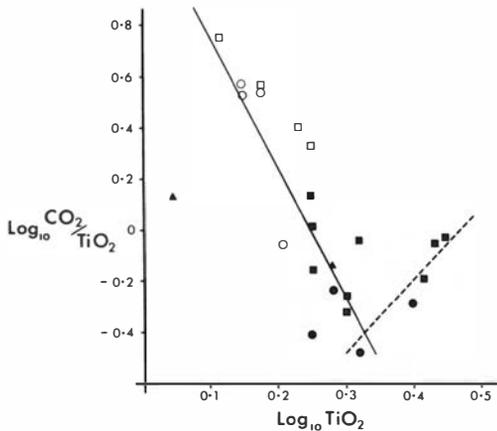
Fig. 1. Log CO_2/TiO_2 against Log TiO_2 plot for the Benna greenstones. The solid line is the best fit linear $(r = -0.8445 ; m = -4.95)$ using all the available data except N11–13. N28a and N44. N11–13 and N28a are tentatively assigned to a subsidiary trend (dashed line). Filled squares – massive lavas; filled circles-pillow selvedges; empty squares – pillow cores; empty circles-pillow rims; filled triangles – pillow matrix.

interesting additional features. An indication of the complexity of major element chemistry within these volcanics is the low correlation coefficients in Table 1 (representing 10 massive lavas and 4 pillow cores). Notable features emerging from this diagram are that TiO_2 has high correlations with P_2O_5 and FeO, that CaO clearly relates to CO_2, and that FeO, TiO_2, P_2O_5, MnO, and to a lesser extent Fe_2O_3, comprise a group of oxides which have high correlation coefficients with each other. The latter feature may be explained in two ways; either these correlations have been preserved from those in the original suite of lavas or during the secondary alteration processes these elements, although mobile, behaved coherently. A study of intrapillow geochemical variations provides a possible solution to this problem. Loeschke (1976) has already shown that secondary TiO_2 enrichment in the pillow selvedges is a persistent feature of the seven pillows he studied in the Benna area (and three pillows from the Støren volcanics about 10–15 kilometres to the south). To investigate the nature of these secondary changes, a plot of TiO_2 against P_2O_5 was constructed for all (n = 34) the specimens analyzed by Loeschke (1976), except the pillow matrix N29 and N44. A high correlation coefficient (r = .923) was recorded, so that although the intrapillow changes are a reflection

of the secondary processes, the resultant migration of P_2O_5 and TiO_2 chemistry closely followed the same trend produced by the massive lavas and pillow cores. The possibility then arises that the overall trend is in fact a product of the same secondary processes that produced the intrapillow variations. Indeed, the high intrapillow enrichment factors (concentration of an element in the selvedge/concentration of the same element in the pillow core) of up to 1.5 for TiO_2 and 1.3 for P_2O_5, provide evidence for sufficient TiO_2 and P_2O_5 mobility to produce the main linear trend.

In addition, Loeschke (1976) has already established that a metamorphic "differentiation trend" is produced by plotting SiO_2 and MgO against the differentiation index (Thornton & Tuttle 1960) with the pillow selvedges and matrix occurring in the field of ultrabasic rocks and the remainder of the samples occurring in the basalt field. Clearly, therefore, secondary processes can produce linear trends.

Similar conclusions have been drawn from the study of many other metamorphosed basic sequences (Hellman et al. 1979, Hynes 1980, Donnelly et al. 1980). In the Ascot formation metabasalts of SE Quebec, for example, it has been shown that secondary mobility of Ti, Y and Zr may be attributed to high CO_2 levels in the fluid phase during metamorphism (Hynes 1980). The resulting metasomatic effects were modelled using an equation analogous to that derived for fractional crystallization processes (Allègre et al. 1977). For two elements, a plot of ln C_1/C_2 versus ln C_2 can be used to evaluate D_1/D_2, where D_1 and D_2 are their respective distribution coefficients (D_1 = concentration of element i in fluid phase/concentration of element i in the rock). As the equation governing the metasomatic process is ln $C_1/C_2 = (D_1/D_2 - 1)$ ln $C_2 + A$ where A is a constant, the slope of a line defined on such a graph will enable us to calculate D_1/D_2. It is only advisable, however, to use this method to determine the relative signs of D_i, with positive and negative values indicating leaching and deposition of element i, respectively. A similar approach can be adopted for the Benna greenstones.

A plot of log SiO_2/TiO_2 versus log TiO_2 (not shown here) defines a good line with a slope of -1 for all the specimens, indicating that D_{Ti} is much greater than D_{Si}. As in the case of the Ascot metabasalts, this may result because of the higher SiO_2 contents in the rock compared to
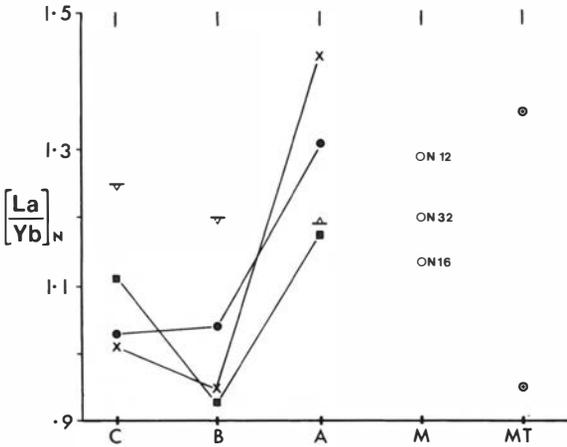
Fig. 2. $(La/Yb)_n$ values for three pillows, three massive lavas and the matrix between two pillows. N denotes chondrite normalized values (Nakamura 1974). C-core, B-inner rim and A-selvedge of individual pillows. Crosses – pillow N21; filled circles – pillow N24; filled squares – pillow N46. M and open circles – massive lavas N12, N16 and N32 (Loeschke 1976). MT and circle with dot – matrix between pillows; N44 – lower values; N29 – higher values. Bar, open triangle – limits of maximized errors for pillow N21.

TiO_2 rather than lower SiO_2 concentrations in the fluid phase. It indicates, however, that in common with the Ascot formation, the effective mobility, of SiO_2 and TiO_2 has been reversed compared with the normal situation.

The importance of CO_2 in the fluid phase is revealed by a plot of log CO_2/TiO_2 versus log TiO_2 (Fig. 1). The significant linear correlation with slope of -2.892 indicates that one of these elements was being leached while the other was being deposited. This is clearly the case for the pillow cores and rims, which have abnormally high CO_2 values (up to 7.4 wt.%) and low TiO_2 contents (lower than 1.3). In addition, three of the massive lavas do not appear to correlate with the main linear trend. A possible explanation for this is that compositions of these lavas define a second linear trend (Fig. 1) with a positive slope. This would indicate that both CO_2 and TiO_2 were either deposited or leached; in view of the very high TiO_2 contents of these rocks and in two cases high CO_2 (N11 and N12), the former is the most probable. In addition, extrapolation of the two alteration trends to a common origin enables one to infer what the initial igneous composition may have been (Fig. 1, Hynes 1980). It should be noted, however, that although the importance of the main trend is marked, the paucity of data

points ensures that the presence of a second trend is at best very speculative.

The existence of linear geochemical trends produced by metasomatism provides evidence that the mobility of some major and trace elements was controlled by their systematic addition to or removal from the Benna greenstones. The importance of CO_2 in the fluid phase is also attested to by its anomalously high concentrations in the pillow cores and rims. However, unlike the Ascot formation, the calcite-rich components of the Benna greenstones are TiO_2 poor. Therefore, although CO_2 in the fluid phase may have enhanced the mobility of TiO_2, by the formation of carbonate complexes, calcite-bearing mineral assemblages did not provide suitable mineral sites for the incorporation of TiO_2.

REE geochemistry

Intrapillow

Loeschke & Schock (1980) have already noted that REE are enriched within the selvedges of these pillows. In accordance with many workers (Terrell et al. 1979, Menzies et al. 1980), this intrapillow geochemical variation was interpreted as being of secondary origin. Subsequent study of Loeschke's (1976) geochemical data by the present author has revealed that REE fractionation has accompanied these variations in REE concentration. In order to show this, normalized La/Yb, La/Sm and Sm/Yb ratios have been calculated for the massive lavas and the three main components of individual pillows. These ratios show significant and systematic variations. Within each pillow the selvedges are enriched in the lighter REE, while the inner rims are relatively depleted (Fig. 2). The massive lavas have higher ratios than both the pillow cores and inner rims, but are either lower than or overlap those of the selvedges.

Loeschke & Schock (1980) published the average errors of all their determinations as an error bar on chondrite normalized REE distribution curves. These errors were maximized for the three REE ratios, and those for La/Yb in pillow N21 are shown in Fig. 2. Clearly, the three components of this pillow have systematic differences in La/Yb ratios (the patterns produced for La/Sm and Sm/Yb ratios are very similar). Although error bar overlap does occur to varying degrees for pillows N24 and N46, their striking similarity
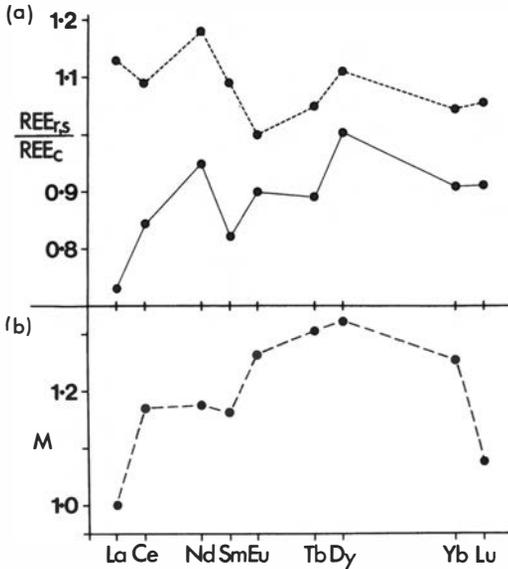
Fig. 3. (a). Mean REE core/REE inner rim (dashed line) and REE core/REE selvedge (solid line) values for the three Benna greenstone pillows.
(b). Normalized slopes (M) of the fractionation lines for La against each REE. The fractionation lines are best-fit linears using geochemical data for the massive lavas and pillow cores (see Table 3).

Fig. 4. La-Yb ppm diagram for the Benna greenstones. Dashed line – fractionation line. Error bars for La and Yb are shown (see N12). Symbols as for Fig. 2.

with N21, for all three REE ratio patterns, suggests that real systematic variations in REE ratios are a feature of all these pillows. As the ratios would otherwise remain constant, it is apparent that REE have been fractionated by the secondary alteration processes. The result of this fractionation is that high LREE/HREE ratios are recorded in the REE-rich selvedges while low ratios occur within the REE-poor inner rims.

As the pillow cores have REE concentrations and ratios of intermediate value relative to the two other pillow components and because the REE composition within each pillow prior to alterations was probably homogenous (Moore 1965), a qualitative measure of the mobility of each REE can be established by comparing the REE core/REE selvedge ratio with the REE core/REE inner rim ratio. The convergence of the curves for these ratios towards HREE (Fig. 3a) indicates that either more LREE were susceptible to chemical transfer than HREE or that LREE were inherently more mobile than HREE during the secondary processes which affected these pillows.

The first alternative arises from the fact that the igneous crystallization history of these lavas
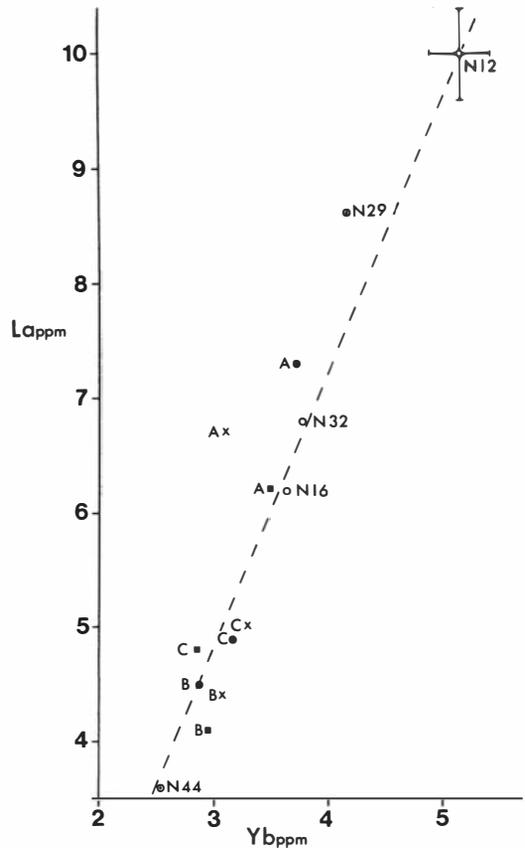
may have controlled the potential mobility of REE (and some major elements, TiO_2 and P_2O_5 in particular). In other words, the crystallizing phases within any lava control the sites of concentration and relative distribution of REE before the intervention of subsequent secondary processes. These phases normally have low REE partition coefficients so that REE are concentrated in the residuum which in many cases is quenched to form a glass. If, as is the case for clinopyroxene and orthopyroxene, the crystallizing phase has a higher partition coefficient for HREE than LREE, then not only will the quenched glass be REE rich but it will also have a LREE/HREE ratio higher than the rest of the pillow. As secondary REE transfer within basic volcanics is considered by many authors to be restricted to or much better developed within the more easily altered glasses (Humphries et al.

Table 2:   Data for normalised (see text) secondary fractionation
lines in La - REE ppm diagrams. m, r are the slopes
and correlation coefficients for the lines produced
by the three massive lavas and three pillow lavas.
r_1 is the correlation coefficient for similar lines
using all the available geochemical data from the
Benna lavas (n = 14).

	La	Nd	Sm	Eu	Tb	Dy	Yb	Lu
m	1.167	1.175	1.163	1.267	1.305	1.323	1.255	1.084
r	0.99	0.89	0.99	0.99	0.98	0.92	0.99	0.95
r_1	0.97	0.84	0.98	0.91	0.95	0.63	0.94	0.91

1978, Frey et al. 1974), their composition will provide some control on the subsequent mobility of REE. In this way, REE-poor domains will have lower LREE/HREE ratios than REE-rich domains, as observed within the Benna greenstones.

The second alternative, that LREE were inherently more mobile than HREE, arises from recent observations that LREE can be preferentially mobilized in some basic volcanics (Wood et al. 1976, Hellman et al. 1979) and preferentially enriched, due to a reaction with a fluid phase possessing a fractionated REE profile, in others (Ludden et al. 1979). These possibilities will be discussed in a later section with particular reference to the Benna greenstones.

Massive and pillow lava interrelations

A treatment of the geochemical data for the massive lavas and pillowed lavas is necessary in order to establish whether any trends that result are of primary or secondary origin. Loeschke & Schock (1980) have previously noted that the REE distribution curves (curves produced by dividing the concentration of each REE in a sample by its mean concentration in selected chondrites) for all the specimens analysed from the Benna lavas are sub-parallel. This feature is analogous to that produced by fractional crystallization where sub-parallel distribution curves result, only differing in the total REE concentrations, the later fractions being enriched in REE (Barberi et al. 1975). In the case of the Benna volcanics, however, even the altered intrapillow distribution curves are parallel. This pattern is similar to that described in a number of volcanic complexes, where secondary alteration processes have produced REE patterns which mimic those

of fractional crystallization. In one case, although REE were mobilized during the hydrous burial metamorphism of some Australian basalts, they behaved remarkably coherently, preserving the form of REE distribution curves (Menzies et al. 1980, Hellman et al. 1979). As they had established that REE were mobile within pillows during secondary changes and because REE concentrations decreased from the less altered massive lavas through pillow lavas to the most altered sample (N44 pillow matrix), Loeschke and Schock invoked a secondary origin for these REE patterns. The discussion that follows provides a more detailed analysis of their geochemical data and reveals some added features of the REE geochemistry of these rocks, the significance of which is briefly discussed.

The relation between the REE geochemistry of the massive lavas and pillows can be studied by plotting La ppm against Yb ppm (Fig. 4). The least squares best fit line for the three massive lavas is closely bounded by data points for the pillows and pillow matrix. Although Barberi et al. (1975) have previously interpreted this type of linear trend as being a clear indication of crystal fractionation, similar patterns have even been observed in metasomatised quartzites which were originally REE free (Martin et al. 1978). Indeed if one plots data from other metabasalts which have undergone coherent REE mobility, they too produce a linear trend.

In the case of the Benna greenstones it is notable that the trend produced does not pass through the origin, so that the La/Yb ratio changes. Massive lava N12 has the highest La and Yb contents while N44 (pillow matrix) the most altered sample (Loeschke & Schock 1980) has the lowest. Very similar patterns result when La is plotted against all other REE. These linear

trends can be compared by multiplying the analyses for each REE by a common factor, such that the contents of all the REE in N12 are normalized to 10 ppm (N12 is chosen because it has the highest REE contents). Data for these lines are presented in Table 2 and it is clear that in each case high correlation coefficients occur. A notable feature to emerge from this exercise is that the slopes of these lines vary from LREE to HREE, in particular a marked increase occurs for Eu and the other HREE (Fig. 3b). This suggests that the process that produced the main linear trends, whether it is a primary igneous or secondary alteration effect, selectively fractionated LREE relative to HREE. This is the same conclusion established from a study of the intrapillow REE geochemistry; indeed La to REE diagrams using all the available analyses show very significant correlations (Table 2) such that the REE compositions of all the pillow components lie along the main linear trend. Another method of illustrating the same feature is to calculate the (REEc/REEr–REEc/REEs) values for each element (see Fig. 3a) and multiply these by a common factor such that the La value is normalized to 1. The resultant values are then plotted against M (the slope of La to REE graphs, Table 2) for each REE. A linear plot results with a reasonable correlation coefficient ($r = 0.80$); however if Lu is deleted (because of its unusually low M value, low concentrations and high analytical errors) a very good fit results ($r = 0.96$). The significance of this is that if both systems had a different relative effect on REE, a linear plot should not be observed. Therefore, if two distinct processes· (primary and secondary) produced the REE fractionation lines and the intrapillow REE variations, they both had similar effects on the relative behaviour of REE. However, another possibiiity exists, that the REE patterns within these rocks were produced by the same secondary alteration process.

Discussion

It has already been established that the major element geochemistry of the Benna greenstones can be produced by metasomatism. The resulting secondary linear trends (Fig. 1) attest to the importance of CO_2 in the fluid phase and the post crystallization mobility of TiO_2. As REE have a high correlation coefficient with TiO_2, they have both behaved in an analogous manner.

This is also suggested in a plot of Log TiO_2/100La versus Log La where a good linear trend ($r = - 0.6818$) with a low slope ($m = - 0.2624$) indicates that both La and TiO_2 were either leached or deposited during the metasomatic process. Although this implies that the REE and TiO_2 fractionation lines are of secondary origin, it does not obviate the possibility that primary igneous characters had some control on their form.

The first possible suggestions that an igneous process has had some role in the subsequent mobility of elements are the REE fractionation lines. They, and the intrapillow REE geochemistries, indicate that either LREE were inherently more mobile then HREE or that more LREE were susceptible to secondary transport in a fluid phase.

The latter argument can be developed further by considering the importance of the igneous crystallization history in basic volcanics. The crystallization of basic lavas on extrusion often produces REE and, in particular, LREE-rich residual glasses (Humphries et al. 1978, O'Nions et al. 1973). If, as is commonly believed, the secondary mobility of REE is restricted to or better developed within the more easily altered glasses (Frey et al. 1974), then more LREE will be susceptible to secondary redistribution. In addition, if the main linear trend between the massive lavas and pillow lavas was produced by fractional crystallization of certain phases and these minerals continued to crystallize out when the lavas had extruded, then the interstitial glasses would have compositions lying along the main primary trend. Subsequent redistribution of REE derived primarily from the easily altered glasses could produce the observed intrapillow REE variations with the three pillow components still adhering to the primary fractionation line.

The suggestion that the main linear trend could be the manifestation of a primary fractionation line can be tested. It should be noted, however, that although various techniques have been applied in the study of primary igneous processes, the prerequisites for sampling are such that almost no published data are suitable. The Benna greenstones are a good example both because they were not sampled expressly for such a systematic treatment and because it is clearly established that they have undergone a very significant degree of secondary alteration. A preliminary test is possible, however, by plotting the Log La against the Log of other incompatible

Table 3:   Correlation coefficients (r) for best fit linear trends produced in plots of Log La versus Log (other elements). D - the calculated bulk partition coefficients for each element.

	TiO_2	P_2O_5	Sc	Sm	Eu	Tb	Yb
r	0.95	0.97	0.72	0.97	0.98	0.99	0.98
D	0.14	0.17	0.61	0.22	0.30	0.32	0.29

elements (elements with an affinity for the residual liquid, for example TiO_2, P_2O_5 and other REE). This method applies the Rayleigh distillation law to trace element behaviour in a fractional crystallization sequence. The linear plots which result can be used to derive bulk partition coefficients (D_i) for individual elements and, in turn, the mineralogical composition of the cumulates (Allègre et al. 1977).

Modelling of these data is difficult, however, because D_{Sc} is so small, suggesting that clinopyroxene was not an important crystallizing phase (Table 3). This does not concur with the important LREE fractionation already established for these greenstones. Indeed, even if one uses low and high clinopyroxene–melt coefficients (Schilling et al. 1978) for scandium and REE respectively, a significant amount of apatite crystallization (up to 0.4%) is required to produce the observed REE contents. The low value for D_p, however, suggests that apatite was not a significant crystallizing phase. It is apparent, therefore, that although the Benna greenstones were not systematically sampled for detailed petrological studies, the main linear trends do not represent primary igneous fractionation lines.

It is possible, however, to produce a model for the formation of the observed trace element and REE geochemical trends based primarily on metasomatic processes. It has previously been shown that element mobility will adhere to the Rayleigh distillation law assuming that the fluid phase is saturated with the elements concerned and that the mass of the rock is held constant during a progressive metasomatic process (Hynes 1980). This model, when applied to the Benna greenstones, affords a good explanation for the depleted concentrations of TiO_2 in the pillow cores and rims. In addition, the high positive correlation between TiO_2 and REE, P_2O_5, Hf and Sc suggests that these elements behaved coherently and were all mobile during metasomatism.

The post crystallization mobility of these normally "immobile" elements may be attributed to high CO_2 levels in the fluid phase (Hynes 1980). This condition facilitates the formation of high order carbonate complexes with high valence cations, without effecting the solubility of lower valence cations. In this environment, trace elements and rare earth elements which have high valences would be more mobile than in one where the metasomatic fluid was aqueous. It is more difficult, however, to explain the preferential mobility of LREE relative to HREE. Although recent work has shown that LREE, in particular La, are sometimes chemically more mobile than HREE during secondary alteration processes (Furnes 1978, Wood et al. 1976), it has also been suggested that under certain conditions a CO_2 rich fluid may have the opposite effect (Herrmann 1970). In contrast, however, LREE enrichment within the more easily altered residual glasses may afford a simpler explanation for their greater mobility.

The alteration trends proposed here are in good agreement with previous observations that the pillow lavas and, in particular, pillow matrix (N44) are more altered than the massive lavas (Loeschke & Schock 1980). However, in the case of the pillow matrix, although trace and rare earth elements have been leached, no concomitant deposition of CO_2 is recorded (Fig. 1). Another problematical feature is whether a subsidiary trend is present on the plot of Log TiO_2/CO_2 against Log TiO_2 (Fig. 1). Although the lack of data points ensures that its presence is speculative, it is notable that if it does exist, the intersection of both trends, at around the compositions of massive lavas N16 and N32, should be closer
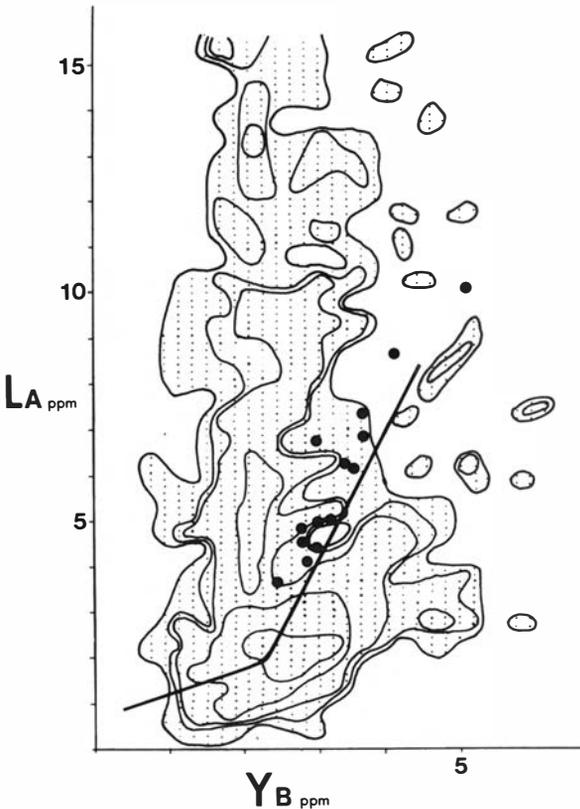
Fig. 5. Contoured La – Yb discriminatory diagram representing 630 recent basalts. Contours were prepared by counting the number of data points within circles of 1/2ppm diameter centered on a 1/4ppm grid. Contoured intervals (%), 0.16: 0.32: 0.64: 1.60: 4.80. Solid line marks the lower boundary of island arc basalts (97% of 148 island arc basalts lie above this line). Solid circles – Benna greenstones.

HREE by the same metasomatic processes. It is apparent, therefore, that the presence of significant inter-element correlations in metamorphosed basic sequences should not be automatically accepted as being of primary origin. In addition, the secondary fractionation of REE has some significance with regard to the use of REE ratios as geotectonic indicators (see Loeschke & Schock 1980). To illustrate this, a contoured La-Yb discriminatory diagram has been constructed by the author, representing data from 630 recent basalts of midocean ridge, 'within plate' and island arc affinities. A bimodal distribution of points is evident with essentially N-type MORB in the La-poor domain and E-type MORB, 'within plate' and island arc basalts in the other (Fig. 5). This diagram illustrates the considerable spread in basalt La–Yb compositions and shows that REE are of limited use when attempting to assign the Benna greenstones to any specific geotectonic environment.

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to the primary igneous composition (Hynes 1980).

Conclusions

The distribution of trace and rare earth elements within the Benna greenstones is attributed to metasomatism by a CO_2 rich fluid phase. Within the more altered pillows, normally "immobile" elements have been depleted with a concomitant increase in CO_2 contents. The resulting linear trends, although similar to those produced by fractional crystallization, attest to the coherent mobility of trace and rare earth elements during metasomatism. In addition, they also indicate that LREE have been fractionated relative to

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