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INFLUENCE OF ROCK CRYSTALLISATION HISTORY UPON SUBSEQUENT LANTHANIDE MOBILITY DURING HYDROTHERMAL ALTERATION OF BASALTS*

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ABSTRACT

Humphris, S.E., Morrison, M.A. and Thompson, R.N., 1978. Influence of rock crystallisation history upon subsequent lanthanide mobility during hydrothermal alteration of basalts. *Chem. Geol.*, 23: 125–137.

Rare-earth element (REE) distributions in individual eruptive basaltic units from eastern Iceland, Mull and the Mid-Atlantic Ridge are presented in order to determine the mobility of these elements during hydrothermal alteration. The factors that cause the light REE (La, Ce and Nd) to be mobile in some cases and not in others are considered. It is postulated that the main control on potential lanthanide mobility is the igneous crystallisation history of the individual lavas, because this affects the sites of concentration, and hence availability, of the REE during hydrothermal alteration. The subsequent importance of the nature of the secondary minerals which form in determining which elements remain in the system is also discussed.

INTRODUCTION

The high geothermal gradients and permeabilities which characterise active eruptive centres provide ideal conditions for the circulation of hot fluids through fresh basalts. Such a process results in metamorphism of the lavas shortly after eruption, and the circulating solutions provide optimum conditions for element transport. Examples of interaction between basalts and hot fluids have been described from mid-ocean ridges (e.g., Miyashiro et al., 1971; Humphris and G. Thompson, 1978 a, b), ophiolites (e.g., Gass and Smewing, 1973; Spooner and Fyfe, 1973), fissure-erupted subaerial lava fields (e.g., Walker, 1970, 1974), and volcanoes (e.g., Fujishima and Fan, 1977). The mineral assemblages developed are, in most cases, typical of the

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zeolite and greenschist metamorphic facies. Data from currently active geothermal areas indicate that alteration takes place at temperatures of up to about 300°C. (e.g., White and Sigvaldason, 1962; Brown and Ellis, 1970; Tomasson and Kristmannsdottir, 1972), which is consistent with the reaction temperatures obtained from metamorphosed oceanic rocks (Muehlenbachs and Clayton, 1972; Wenner and Taylor, 1973). The fluid/rock ratios in these geothermal systems are extremely variable (e.g., Mottl et al., 1975; Spooner et al., 1977 a, b), but intense hydration and carbonation of the rocks is generally observed.

In recent years, the chemical changes in basaltic rocks subjected to hydrothermal metamorphism have been much studied. Interest has focussed upon element mobility and its role in geochemical mass balances (e.g., Humphris and G. Thompson, 1978a) and ore genesis (e.g., Graf, 1977), and on attempts to decipher the pre-metamorphic chemistry of the basalts (e.g., Condie and Baragar, 1974). Certain elements, such as Ti, P, Zr, Hf, Nb, Ta and Y have been shown to be comparatively immobile, except during extreme metasomatism (e.g., Herrmann et al., 1974; Smith and Smith, 1976). Other elements, such as Li, K, Rb, Sr, Ba and U appear to be mobile (e.g., Vallance, 1974; Gunn and Roobol, 1976; Wood et al., 1976).

In this paper we concentrate on the rare-earth elements (REE) for which evidence of mobility during hydrothermal alteration is controversial (e.g., Herrmann and Wedepohl, 1970; Haskin et al., 1971; Frey et al., 1974; Tanaka, 1975; Ferrara et al., 1976; Menzies, 1976; Wood et al., 1976; Floyd, 1977; Hellman and Henderson, 1977). Using the published results of Wood et al. (1976) for eastern Iceland, and new data, obtained by the same method (Wood et al., 1976, p. 242), for Mid-Atlantic Ridge pillow basalts and Mull lavas, we shall compare the REE mobility in these three hydrothermal systems, and attempt to elucidate the reasons why the light REE (La, Ce and Nd) are mobile in some instances and not in others.

It is essential to emphasize that the three examples to be discussed are all concerned with chemical changes within *individual eruptive units* (flows or pillows) of basalt. Recent geochemical studies of unmetamorphosed basaltic suites, which are based on abundant analytical data, show considerable unit-by-unit diversity in chondrite-normalised REE pattern slopes (Sun and Hanson, 1975; O'Nions et al., 1976; Puchelt and Emmermann, 1977). It therefore seems improbable that attempts to study possible large-scale lanthanide mobility by comparing sets of analyses from unmetamorphosed and metamorphosed lava successions will be able to separate pyrogenic from subsequent variation.

EASTERN ICELAND

A 10 km thickness of predominantly basaltic flows is exposed in eastern Iceland. These have formed mainly by subaerial fissure eruptions during the separation of the European and North American lithospheric plates since approximately 14 Ma. The flows dip gently westwards and are cross-cut by

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sub-horizontal zeolite facies metamorphic zones. Local greenschist hydrothermal aureoles surround several buried Tertiary centres of abundant acid/intermediate volcanism — analogues of the currently active central volcanoes in the Neovolcanic Zone (Walker, 1974). Wood et al. (1976) studied element mobility resulting from the zeolite facies regional metamorphism. They compared chemical variations across a post-glacial basalt on the Reykjanes peninsula, SW Iceland, with a zeolitised Tertiary flow from Reydarfjordur, eastern Iceland.

Reykjanes flow

This 4.5 m thick basalt flow lacks a soil cover and is therefore probably no more than a few hundred years old. It contains several percent of subhedral olivine, augite and plagioclase phenocrysts with variable distributions. The groundmass consists mainly of equant granular augite intergrown with plagioclase laths, sparse subhedral Fe—Ti oxides, and rare olivine. The abundant spaces between the groundmass grains are filled with pale brown glass, which contains numerous, indeterminate $< 2 \mu\text{m}$ opaque and translucent crystals.

Chemically, this lava is a typical Icelandic *hy*-normative olivine tholeiite with 7.6–8.0% MgO. A suite of twelve specimens from a vertical section through the flow revealed little variability for any elements (Wood et al., 1976, table 3). Moreover, such variation as was observed could be attributed entirely to varying concentrations of the three phenocryst phases. REE data are summarised in Fig. 1, which shows the chondrite-normalised patterns with the highest and lowest values of ΣREE and $(\text{Ce}/\text{Yb})_N$ ratios. It is apparent that the light rare-earth elements (LREE) display no greater variability than the heavy rare-earth elements (HREE).

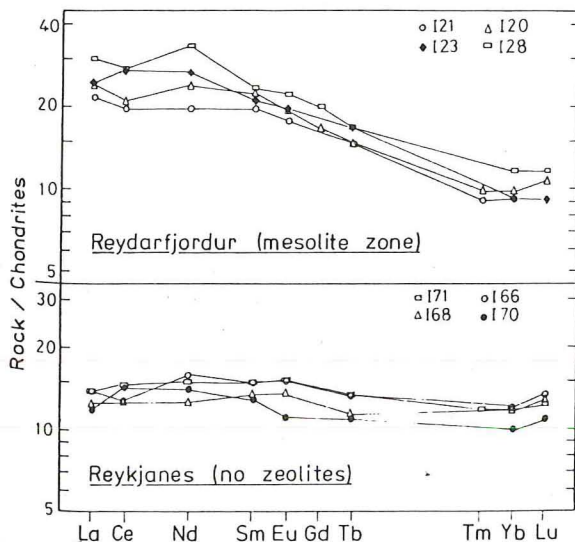


Fig. 1. Chondrite-normalised REE patterns for basalts from a Recent flow from the Reykjanes peninsula, and from a zeolitised flow, Reydarfjordur, eastern Iceland. (Data from Wood et al., 1976.)

Reydarfjordur flow

This 20.5 m thick basalt flow is about 12 Ma old. It lies within the meso-lite zeolite zone of Walker (1974) and contains this mineral, together with abundant stilbite, infilling prominent vesicles at the top and bottom of the flow. Zeolites and submicroscopic green and brown ferromagnesian minerals also fill the small vesicles throughout the lava and are disseminated within the rock. Sufficient of the pre-metamorphic mineralogy of the lava is preserved to see that it closely resembled the Reykjanes basalt petrographically. A few percent olivine, augite and plagioclase phenocrysts were present, with abundances varying little throughout the flow. The groundmass is rich in granular augite but the interstitial glass patches have all been converted to fine-grained assemblages of zeolites and hydrated ferromagnesian minerals.

The intensity of hydrothermal alteration depends on the original vesicularity of the lava. Thus it is greatest at the flow margins but also varies considerably in the interior. Zones with maximum alteration show, in addition to recrystallisation of the glass, complete replacement of olivine and incipient conversion of plagioclase to hydrous minerals. The augite, however, remains intact.

Chemically, this lava is a *hy*-normative olivine tholeiite with 6.0–7.2% MgO. Wood et al. (1976) compared the chemical variation of twelve samples from a vertical section through this flow with that of the Reykjanes lava. Variability greater than could be explained by phenocryst distribution or analytical error was recorded for Si, Mg, K, Rb, Sr and the LREE. As most of this variation occurred near the vesicular margins of the flow, Wood et al. (1976) attributed it to different elemental mobility during zeolite facies metamorphism. REE data, represented by the patterns with highest and lowest values of Σ REE and $(Ce/Yb)_N$ ratios, are summarised in Fig. 1.

MULL, NW SCOTLAND

In Mull, Tertiary lavas reaching a thickness of up to 1850 m cover an area of about 840 km². The lower part of the pile consists mainly of basalts which are chemically and petrographically similar to the Skye Main Lava Series (R.N. Thompson et al., 1972; Morrison, 1978). They are transitional basalts that straddle the critical plane of silica saturation — the normative “join” olivine–clinopyroxene–plagioclase — and vary from nepheline to hypersthene normative varieties.

Two distinct types of alteration occur in the basalts. A hydrothermal aureole, consisting of an inner epidote and outer prehnite zone, surrounds the central intrusive complex in south and east Mull. Everywhere within this region, $\delta^{18}O$ whole-rock values decrease radially towards the intrusive complex (from about +5‰ to about -5‰) demonstrating that interaction with heated meteoric water has occurred at temperatures up to about 300°C (Forrester and Taylor, 1976). Outside the central aureole, flat-lying zeolite facies zones, that essentially parallel the base of the lava pile, occur.

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Most of the basalts lie in the laumontite zone, only the top 200 m of which is exposed in Iceland (Walker, 1970). These Mull basalts have "normal" igneous $\delta^{18}\text{O}$ values (+9‰ to +5‰), indicating temperatures sufficiently low for the water to have $\delta^{18}\text{O}$ values required for isotopic equilibrium between plagioclase and water — between 100 and 150°C (Forrester and Taylor, 1976).

To estimate the metasomatic effects of these two types of alteration on the REE contents, two lava flows have been studied — one from the laumontite zone, and one from the epidote zone within the central aureole.

Zeolitised lava

This lava is exposed in a quarry in SW Mull and contains olivine, large poikilitic titanogites, subpoikilitic titanomagnetites, chlorite, and zeolites. Rare apatites are enclosed in the pyroxenes. The secondary alteration is concentrated mainly at the base of the flow where an amygdaloidal layer lies immediately above the bole, and zeolite-filled vesicle pipes, up to 1 m in length, penetrate vertically into the flow. Petrographically, these can be seen to cause some serpentinisation of the olivine, partial replacement of plagioclase by hydrous minerals and the growth of small patches of chlorite and zeolites in the groundmass.

Little chemical change is seen across this flow, other than slight variations in Sr content and variable ferrous/ferric ratios. REE patterns for two examples are shown in Fig. 2. Sample *M53* is from the non-vesicular flow cen-

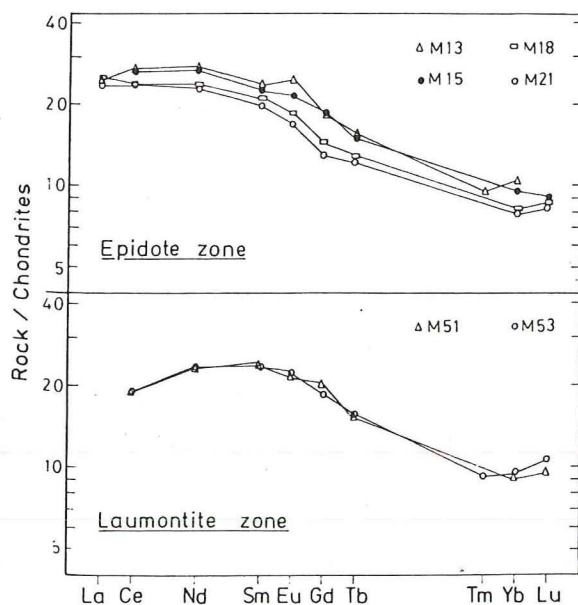


Fig. 2. Chondrite-normalised REE patterns for altered basalts from Mull. (*M53* and *M51* are from the zeolitised lava; *M13*, *M15*, *M18* and *M21* are from a flow in the epidote zone.)

tre, and *M51* is from the pipe vesicle zone. These two patterns are virtually indistinguishable.

Epidote zone

This lava flow is exposed in a quarry 3.5 km E of Salem, and shows a gradual transition for dark rock in the centre of the flow to green "spilitic" rock at the margin. Originally, it consisted of olivine phenocrysts in a matrix of olivine, plagioclase, titanomagnetite and poikilitic augite. In the dark centre of the flow, only olivine has broken down. This is pseudomorphed by chlorite and Fe-oxides, and the groundmass is rich in chlorite. As the margin of the flow is approached, plagioclase is albitised and growth of calcite and epidote occurs. Only at the margin of the flow is pyroxene broken down and an assemblage of chlorite, albite, quartz, carbonate, epidote, Fe-oxides, and amphibole has formed. Within this flow, Ti, Zr, Y, Nb and P preserve constant ratios, except at the margin where slight loss of P occurs (Morrison, 1978). This is accompanied by variations in Na₂O, K₂O, MgO, SiO₂, Rb, and Sr, and drastic leaching of CaO as the margin is approached.

Four REE patterns from the flow are shown in Fig. 2, and summarised data are given in Table I. Sample *M13* is from the green flow margin, and samples *M19*–*M21* are from the dark flow interior. The slopes of the patterns, as expressed by (Ce/Yb)_N, are constant, and there is no change in abundance of the LREE relative to the HREE, except in sample *M13*. There is, however, an apparent increase in total abundance of most of the REE progressively from the least altered to the most altered parts of the flow.

TABLE I

Selected rare-earth and trace element data from the altered lava flow in the epidote zone, Mull

Sample*	Ce (ppm)	Yb (ppm)	(Ce/Yb) _N	TiO ₂ (wt.%)	Y (ppm)
<i>M13</i>	23.64	2.29	2.63 ± 0.11	1.61	28
<i>M14</i>	22.53	2.01	2.86 ± 0.07	1.54	24
<i>M15</i>	23.28	2.08	2.83 ± 0.06	1.45	22
<i>M16</i>	22.56	1.99	2.87 ± 0.07	1.39	20
<i>M17</i>	19.93	1.71	2.95 ± 0.06	1.34	20
<i>M18</i>	19.96	1.73	2.92 ± 0.07	1.39	21
<i>M19</i>	20.20	1.69	3.02 ± 0.06	1.34	21
<i>M20</i>	20.23	1.88	2.72 ± 0.08	1.35	21
<i>M21</i>	20.25	1.71	3.00 ± 0.09	1.38	21
<i>M22</i>	19.51	1.80	2.76 ± 0.09	1.40	24

*Sample numbers increase progressively towards the dark flow interior (*M19*–*M21*). *M22* shows the beginning of changes approaching the lower margin, which lies below the quarry floor, as has been proved by drilling.

MID-ATLANTIC RIDGE BASALTS

The basalts analysed in this study were dredged from the median valley of the Mid-Atlantic Ridge at 22°S. The four samples discussed here are pillow basalts that show zoning due to partial greenschist facies metamorphism of the outer pillow margins during reaction with a circulating, seawater-derived fluid. The distinct zoning displayed by these rocks allowed portions of the altered rims and the relatively fresh interiors of the same pillows to be separated for analysis.

The mineralogy and the mineral conversions during alteration of these basalts have been extensively discussed previously (Humphris and G. Thompson, 1978a). The interiors of these pillows have the typical mineralogy and textures of oceanic tholeiites. Briefly, they are composed dominantly of glass (generally 60–70% by modal analysis) containing microphenocrysts and microlites of plagioclase (An_{60-70}), and rare olivine. Fe-oxides are extremely fine-grained and are scattered throughout the groundmass. The altered rims show the characteristic greenschist facies mineralogy of albite—actinolite—chlorite—epidote, with the dominant mineral being a ripidolitic chlorite (up to 60% by modal analysis). However, the outer rim of the most highly altered sample (*AII-42 1-96*) is composed dominantly of quartz and chlorite with no actinolite and only 15% modal albite. In all the samples, the glass is replaced by chlorite which is sometimes intergrown with actinolite. Chlorite also forms pseudomorphs after olivine, which are commonly associated with euhedral pyrite. The plagioclase is albitised and, in some cases, altered to chlorite. The vesicles are generally filled with chlorite although, in the more altered samples, they are lined with quartz and then subsequently filled with chlorite.

Considerable mobility of many of the major and trace elements during hydrothermal alteration has been observed (Humphris and G. Thompson, 1978a, b). In particular, Ca, Si, Cu, and Sr are leached from the rock, while Mg and H₂O are taken up. Mobilisation of Fe, Mn, B, Li, Ba, Ni, and Co is also indicated, but Ti, V, Y, Zr and Cr do not appear to be affected by hydrothermal alteration.

REE data for the fresh and altered zones of each pillow are summarised in Table II, and the chondrite-normalised patterns are shown in Fig. 3. Within the analytical error, the HREE display no variability during alteration. However, some small, but significant, variation is observed in the concentrations of the LREE. In particular, higher concentrations of La are observed in the altered zones of *AII-42 1-96*.

DISCUSSION

In discussing the variation in REE abundance within individual eruptive units, it is necessary to distinguish between *real* changes in concentration and *apparent* differences due to leaching or addition of other elements.

TABLE II

Selected rare-earth and trace element data from partially altered pillow basalts from the Mid-Atlantic Ridge (22° S).

Sample*	Ce (ppm)	Yb (ppm)	(Ce/Yb) _N	TiO ₂ (wt.%)	Y (ppm)
AII-42 1-96A	8.77	3.27	0.68 ± 0.03	1.40	35
	8.02	2.89	0.71 ± 0.03	1.33	30
	8.57	2.96	0.73 ± 0.02	1.26	39
AII-42 1-97A	10.47	3.53	0.76 ± 0.03	1.46	40
	9.58	3.34	0.73 ± 0.04	1.37	35
AII-42 1-108A	8.88	3.42	0.66 ± 0.04	1.98	45
	9.88	3.02	0.83 ± 0.04	1.43	39
AII-42 1-118A	8.61	3.21	0.68 ± 0.04	1.53	39
	8.60	2.91	0.75 ± 0.04	1.35	38

*A, B, C: zones from a single pillow basalt, from the altered rim (A) towards the relatively fresh interior (B or C).

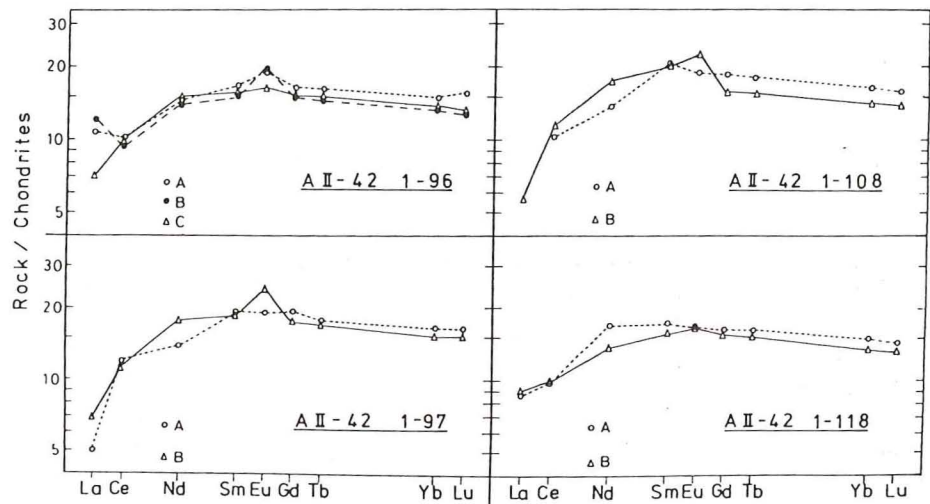


Fig. 3. Chondrite-normalised REE patterns for four partially hydrothermally altered pillow basalts from the Mid-Atlantic Ridge. [A, B, C: zones from a single pillow basalt, from the altered rim (A) towards the relatively fresh interior (B or C).]

Tables I and II illustrate the proportionality between the changes in REE abundances and those of other immobile elements. This suggests that the parallel shifts of the REE patterns that can be seen in Fig. 2, and of the HREE patterns in Fig. 3, can be ascribed to such leaching processes, which

will result in apparent enrichments of the immobile elements. However, taking this into account, we wish to emphasize that the maximum relative LREE movement recorded in the examples of hydrothermal metamorphism considered in this paper is small. This contrasts with the very large alterations to basaltic REE distributions postulated to occur during spilitisation by Hellman and Henderson (1977). Furthermore, it is apparent that the degree of mobility or immobility shown by the REE cannot be related to metamorphic grade.

Solution chemistry also seem unlikely to be the key to the problem. The three areas of study include interaction of basalt with either meteoric or seawater, and yet no obvious distinction in the REE behaviour that can be attributed to solution chemistry can be observed.

We postulate that the *main control on potential lanthanide mobility is the igneous crystallisation history of the individual lavas*, insofar as this affects the sites of concentration and relative distribution of the REE before subsequent metamorphism.

The Iceland and Mull lavas may first be contrasted. The presence of augite among the sparse phenocrysts in the Iceland basalts used in this study indicates that this phase precipitated at liquidus or near-liquidus temperatures. In a basalt devoid of hydrous minerals, all the early-crystallising phases — olivine, plagioclase, and pyroxene — have partition coefficients for the REE of <1.0 . Of these phases, augite has the highest partition coefficients [averaging 0.62 for Yb (Arth, 1976)] for the HREE, but low coefficients [averaging 0.15 (Arth, 1976)] for the LREE. An eastern Icelandic basalt crystallising abundant augite throughout its consolidation will therefore contain a residuum, chilled to glass, which is rich in total REE, and has a high LREE/HREE ratio. The two Icelandic basalts that we have discussed are both comparatively impoverished in P and Zr (Wood et al., 1976), so that the REE-rich phases, apatite and zircon, would, if at all, precipitate very late in their consolidation. We can find no apatite or zircon within the groundmass minerals or interstitial glass patches of these flows. The composition of the interstitial glass patches is, in most cases, rhyolitic (D.A. Wood, pers. commun., 1977) but they are too small to extract for REE analysis. O'Nions and Grönvold (1973) have, however, analysed several Recent Icelandic acid lavas and found them to have $(Ce/Yb)_N$ from 3.2 to 7.4, compared with 0.9–1.9 for associated basalts. The phase in the eastern Icelandic basalts most readily attacked by circulating fluids during hydrothermal metamorphism is the interstitial glass; hence the preferential mobilisation of the LREE.

The zeolitised transitional basalts of Mull and Morvern never contain augite phenocrysts. It occurs only as a comparatively late-stage groundmass phase, usually in relatively large poikilitic crystals enclosing large numbers of small plagioclase subhedra. The restricted precipitation of augite during consolidation greatly reduces the potential of this phase to fractionate the REE in the residuum. Furthermore, the comparatively small number of large augite and occasional Ti-magnetite poikilocrysts in the groundmass of a

given volume of ophitic basalt leave fewer intergranular spaces where residual glass pools can collect than occur in a comparable volume of typical Icelandic basalt. Fresh glass is not uncommon in acid intrusions, basaltic hyaloclastites and dyke selvages in the Hebridean Province (e.g., Bailey et al., 1924). Nevertheless, we know of no examples of fresh interstitial glass within the transitional basalts, and from petrographic studies of the least metamorphosed basalts ($H_2O < 1.0\%$), it appears that these lavas were almost entirely holocrystalline. In the absence of abundant glass, the hydrothermal fluids attacked first the olivine and then the plagioclase; hence the REE immobility. In sample *M13* the breakdown of the poikilitic augite allowed alteration of the enclosed apatite, as is indicated by loss of P (Morrison, 1978), which results in a slight decrease in the LREE abundances.

In contrast to this, the oceanic pillow basalts discussed contain no augite and are composed of up to 80% glass with a very high glass/crystal ratio. The microphenocrysts are dominantly plagioclase, with rare olivine. In comparison with Iceland, this glass is therefore basaltic and will not have been relatively enriched in the LREE during its crystallisation history. Hydrothermal alteration of the pillow basalts has resulted in almost complete replacement of the original mineralogy, and hence any variation in the overall REE pattern will be dominantly controlled by the secondary mineralogy.

This leads into our final point which is that, although rock crystallisation history may largely control relative REE availability during hydrothermal metamorphism, the nature of the metamorphic minerals that form must also influence the extent to which the elements, once in solution, are reprecipitated nearby or pass out of the system. Wood et al. (1976) gave chemical data for thirteen minerals common in the amygdales of zeolite facies metamorphosed eastern Iceland lavas. They comprised nine zeolites, plus apophyllite, aragonite, celadonite, and chalcedony. Only the celadonite contained detectable La (> 1.0 ppm) and even in this phase the REE were in concentrations too low to be measured accurately by the techniques available to these authors. In addition, one of us (M.A.M.) has attempted to measure the REE contents of Mull secondary calcite, but 2.5-day counts resulted in no resolvable peaks.

In contrast, there are suggestions in the literature that albite, epidote, and chlorite, which are all characteristic products of greenschist facies metamorphism, can affect the distribution of selected REE. The conditions under which alteration occurred may affect the distribution of Eu, since it is the only REE that will be stabilised in the divalent state if conditions are mildly reducing. The extent of alteration of the plagioclase may also affect the Eu abundance. Weill and Drake (1973) observed a positive correlation between the Eu concentration and the Ab content of the plagioclase. The Eu contents of the altered rims of the oceanic pillows show small variations relative to the interiors, some of which may be due to variations in the original distribution of plagioclase within the pillow. However, these rocks all contain pyrite, indicating that reducing conditions were prevalent at some time dur-

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ing alteration, and this, together with the variable degree of albitisation of the plagioclase, may result in changes in the Eu content of the altered rims relative to the interiors. Similarly, the margin of the Mull flow from the epidote zone (sample *M13*), which is highly reduced, shows a small change in the Eu content.

Although not found in basaltic rocks, the existence of allanite indicates that LREE can enter the Ca^{2+} sites in members of the epidote group. The uptake of substantial amounts of La by adsorption has been described in Quaternary clay-chlorite mixtures of Norway (Roaldset and Rosenquist, 1971). There is a suggestion that this process may have operated during alteration of the ocean-floor basalts. The outer margin of sample *AII-42 I-96* contains the most chlorite (60%) and also shows enrichment of La relative to its concentration in the interior (Fig. 3). The REE abundances in chlorites from greenschist facies metabasalts are currently being investigated (M.A.M.).

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