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Magmatic differentiation of the least incompatible element enriched lavas from PO-1 segment, 37°N on the Mid-Atlantic Ridge (MAR)

Diferenciação magmática das lavas menos enriquecidas em elementos incompatíveis do segmento PO-1, 37°N na Crista Média Atlântica

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Abstract: PO-1 is a second-order segment from the Mid-Atlantic Ridge, in the Azores region, characterised by E-MORB type magmatism. The existence of a crustal magma chamber in the segment centre provides the setting in which differentiation of magmas can occur. Taking into account only the least incompatible element enriched lavas (sampled along the entire segment) assumed to be originated by melting the ambient mantle (and not the most enriched mantle heterogeneous domains, thought to coexist), insights into the processes of magma evolution are explored.

Keywords: E-MORB, Magma differentiation, Crystal fractionation, Mantle melting, Mineral accumulation.

Resumo: PO-1 é um segmento de segunda ordem da Crista Média Atlântica, na região dos Açores, caracterizado pela existência de magmatismo do tipo MORB-E. A existência de uma câmara magmática crustal no centro do segmento providencia as condições necessárias para que possa ocorrer a diferenciação dos magmas gerados por fusão mantélica. Considerando-se somente as lavas caracterizadas por um menor enriquecimento em elementos incompatíveis (amostradas ao longo de todo o segmento), e assumindo a sua geração por fusão do manto com características geoquímicas regionais (e não por fusão das coexistentes heterogeneidades mantélicas enriquecidas), abordar-se-á o estudo dos processos de evolução magmática.

Palavras-chave: MORB-E, Diferenciação magmática, Cristalização fraccionada, Fusão mantélica, Rochas cumuladas.

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1. Introdution

PO-1 segment (also known by Lucky Strike segment) is located between 37°00' N and 37°35'N on the Mid-Atlantic Ridge, has a total length of ~65 km and is bounded by two second-order non-transform discontinuities. Based on the relationship among several incompatible element and isotopic ratios, PO-1 basalts were previously subdivided into three compositional groups (Ferreira, 2007). The least enriched group has the lowest more-to-less incompatible element ratios and the lowest Sr-Pb, and highest Nd, radiogenic values. In spite of this, the basalts present REE and multi-element patterns typical of E-MORB. They were collected throughout the PO-1 segment, are almost aphyric, exhibit low vesicularity, and are considered as resulting of ambient mantle melting under the influence of Azores hotspot.

Given the existence of a) a crustal magma chamber, 3 km below the seafloor (Singh *et al.*, 2006), which provides the setting in which differentiation of magmas can occur and b) being the PO-1 segment volcanism directly related to this magma chamber, this site provides excellent conditions to study the occurring magmatic differentiation processes, based on the chemistry of the lavas erupted along the segment.

The samples used in this study were recovered during two cruises: TTR-10 (2000) and TTR-12 (2002), both on board of the Russian R/V Professor Logachev. Sampling targets were identified from swath bathymetry, acoustic backscatter and deep-tow high-resolution sidescan sonar (TOBI) data obtained for the Lucky Strike segment during the HEAT cruise (German *et al.*, 1996; Parson *et al.*, 2000). Geographical dispersion, together with the diversified existing acoustic facies, have controlled the sampling locations.

2. Insights into the processes of magma evolution

Crystal fractionation is one of the major processes affecting the compositions of magmas beneath mid-ocean ridges after segregation from the melting region (e.g. Grove *et al.*, 1992). Basalts from the PO-1 segment have their most primitive lavas characterized by Mg#, MgO contents and compatible trace elements (e.g. Ni, Cr) concentrations, below the expected values for magmas derived in equilibrium with a mantle mineralogy. Moreover, these basalts present a considerable range in compositions, implying they must have undergone



Artigo Curto Short Article considerable modification during ascent, prior to eruption (i.e. variable extents of crystal fractionation).

The effects of crystal fractionation can be evaluated through the examination of figure 1, where several elements are plotted against a differentiation index (MgO). However, it is apparent that two samples are systematically plotted outside the different correlation trends obtained. In addition to the distinct chemical characteristics shown by these two lavas, samples 432 and 3397/1A, both are plagioclase phyric, and the volume percentage of this mineral is relatively high (15-45%). Combining both information, together with the fact that the chemical analyses were from bulk rock, it is considered that these two lavas do not represent magmatic liquids but, instead, correspond to plagioclase cumulates.



Fig. 1. Various element concentrations (Na₂O, CaO, Zr and Ni) plotted against MgO contents (which represent a differentiation index) for studied basalts. Note the distinct correlation obtained for incompatible (Na₂O and Zr) and compatible (CaO and Ni) elements. These interelement relationships, coupled with the absolute concentrations of MgO, Ni and Cr, together with the Mg# values obtained (54 – 68), all indicate that fractional crystallization had a major role in the chemical diversity found in the PO-1 segment lavas.

Fig. 1. Diagramas de variação Na₂O, CaO, Zr e Ni vs. MgO (representando o índice de diferenciação) para os basaltos estudados. Notar a distinta correlação obtida para os elementos incompatíveis (Na₂O e Zr) e compatíveis (CaO e Ni). As co-relações elementares obtidas e os valores determinados para os Mg# (54 – 68), indicam que a cristalização fraccionada teve um papel importante na diversidade química das lavas menos enriquecidas do segmento PO-1.

2.1. Mineral accumulation

It is apparent that for plagioclase-phyric lavas the various elements not entering plagioclase crystallographic network (e.g. MgO, Na₂O, Zr, Ce) have considerably lower concentrations relative to the rest of the samples, whereas the essential compositional elements of this mineral, such as Ca and Al, have comparatively higher concentrations. Since the accumulation of mineral phases in the magmas is merely a physical effect, it can be roughly corrected. To perform this, it is necessary to make two assumptions:

1) Both lavas (432 and 3397/1A) are shifted from the fractionation trend just due to pure plagioclase accumulation, which is substantiated by petrographic studies.

2) The distribution coefficients are equal to zero for the incompatible elements in plagioclase.



Fig. 2. Diagram showing the correction procedure used for the plagioclase accumulation using two incompatible elements in plagioclase, MgO and Zr. The correction procedure consisted in recalculating the Zr and MgO concentrations of both two lavas affected by plagioclase accumulation, after removing increments of 1% of cumulus plagioclase. The results obtained (open circles) indicate 38% and 9% accumulation of plagioclase crystals for 432 and 3397/1A samples, respectively. b) Ce vs. MgO showing the effectiveness of the correction performed (open triangles-corrected values).

Fig. 2. Gráfico relacionando dois elementos incompatíveis na plagioclase, MgO e Zr, mostrando a metodologia efectuada para correcção dos efeitos da cumulação da plagioclase. O procedimento consistiu em recalcular as concentrações de Zr e MgO para as duas amostras mostrando sinais de serem cumulados, através da remoção incremental de 1% de plagioclase. Os resultados obtidos (círculos abertos) indicam uma percentagem de acumulação de plagioclase de 38% e 9% para as amostras 432 e 3397/1A, respectivamente. b) Ce vs. MgO mostrando a eficácia da correcção efectuada (triângulos abertos-valores corrigidos).

Assuming this, the percentage of dilution in the concentration of the incompatible elements is directly proportional to the percentage of plagioclase accumulated. Based on this relationship, and considering, for example, a plot correlating two incompatible elements in plagioclase, such as MgO and Zr, it is possible to calculate both concentrations in the magmas prior to plagioclase accumulation. If a certain percentage of cumulus plagioclase were incrementally extracted, the variation on the Zr and MgO concentrations for both elements. The corrected concentrations will be obtained when such trends intersect the differentiation trend established using the rest of the lavas. This procedure is represented in figure 2a, and the results obtained indicate a plagioclase accumulation of 38% and 9%,

respectively for samples 432 and 3397/1A. These percentage values can now be applied to roughly correct the concentrations for the rest of the incompatible elements; however, the associated error of this correction procedure will increase for the elements having progressively higher distribution coefficients in plagioclase. The effectiveness of such accumulation correction was evaluated plotting the corrected concentrations for other elements against MgO (Fig. 2b), obtaining coherent trends, supporting the hypothesis of plagioclase being the only mineral phase to accumulate during magma differentiation.

2.2. Melting degree

Through the examination of figure 3, it is seen that the formed trends attributed to crystal fractionation have their origin in four basalts having identical MgO concentrations but slightly distinct incompatible and compatible element concentrations. These basalts are the most primitive ones from the studied samples, presenting the highest MgO concentrations, and are interpreted to be the result of variable extents of partial melting. This hypothesis finds support on the relationship between La/Yb ratios and MgO concentrations (Fig. 3). La/Yb ratios are relatively insensitive to crystal fractionation but, conversely, strongly dependent on the melting degree, due to distinct bulk distribution coefficients presented by both rare earth elements for the mantle mineralogy. For a very limited MgO variation presented by lava samples 435/1A, 435/1B, 434/1, 432 and 434/2 (between 8.51 and 8.63 wt%) the La/Yb ratios range from 1.8 to 2.6. This is highly significant and should mean that lavas containing the highest La/Yb ratio (e.g. 435/1A) would have been derived by a lower melting degree relative to those having the lowest La/Yb ratio (e.g. 434/2). Thus, and assuming that all these five lava samples have resulted from melting of a relatively homogeneous mantle source, as it holds true according to the trace element and isotopic data (Ferreira, 2007), the lavas originated by lower melting degrees should have higher incompatible element concentrations than those derived by a higher extent of melting, for a given MgO concentration. The chondrite-normalized patterns for all five most primitive samples are shown in figure 4a and generally sustain the afore-mentioned expectations. Moreover, other element ratios (e.g. Nb/Zr, Fig. 4b), being also dependent on the extent of melting show concordant relationships against La/Yb ratios. These geochemical arguments may also be extended to certain major element systematics. Sun et al. (1979) suggested that increasing the degrees of melting of the mantle could produce a progressive enhancement of Al₂O₃/TiO₂, and CaO/TiO₂ in the melts, but at a critical point these ratios would not change. This is simply because Ti is essentially incompatible and Al and Ca are compatible and if the amount of melting increases, the Al-Ca retaining phases in the source become exhausted, and the Al_2O_3/TiO_2 , and CaO/TiO_2 ratios will no longer increase in the resultant melt (Sun et al., 1979). Whereas sample 434/2 has $Al_2O_3/TiO_2 = 20.8$ and CaO/TiO₂ = 17.8, the other four samples present limited, but undoubtedly lower values for the two ratios: 16.4 - 17.0 and 14.2 - 14.4, respectively. In addition, and as expected, the TiO₂ concentration in sample 434/2 is relatively lower (0.78 wt%) than the rest of four primitive samples (0.89 - 0.92 wt%).



Fig. 3. La/Yb ratios plotted against MgO concentrations for PO-1 segment least enriched basalts. This plot emphasizes the role of variable degrees of mantle melting in generating the chemical characteristics presented by the most primitive lavas. A significant variation in La/Yb ratios occurs for just a slight variation in the MgO concentrations for the five most primitive lavas (black circles).

Fig. 3. Diagrama de variação La/Yb vs. MgO para os basaltos menos enriquecidos do segmento PO-1, dando ênfase ao papel importante que o grau de fusão parcial terá tido na génese das características químicas apresentadas pelas lavas mais primitivas. Notar a variação significativa nas razões La/Yb para um intervalo restrito nas concentrações de MgO das lavas mais primitivas (círculos negros).



Fig. 4. a) Chondrite-normalized REE concentrations for the most primitive lavas. To note the remarkably constant normalized concentrations for LREE (e.g. \sim 18 for La) as opposite to those more variable obtained for the HREE. b) Nb/Zr vs. La/Yb plot produce well correlated trends for the five most primitive samples (black circles).

Fig. 4. a) Padrões de terras raras normalizadas em relação aos condritos para as lavas mais primitivas. Notar as idênticas concentrações normalizadas obtidas para as terras raras leves (e.g. ~ 18 for La) em oposição à variabilidade existente para as terras raras pesadas. b) Diagrama Nb/Zr vs. La/Yb com elevada correlação para os cinco basaltos mais primitivos (círculos negros).

The variable extents of melting needed to explain the chemical characteristics of the most primitive lavas could be related to the depth range of melting in the mantle source. A particular useful element ratio, and frequently used as an indicator of the mean depth of mantle melting, is the Gd/Yb which is a measure of the fractionation between middle and heavy REE. This ratio can be significantly affected if garnet is residual in the mantle mineralogy since this silicate retains the heavy REE other than the middle REE (such as Gd) (e.g.

Hellebrand *et al.*, 2001). Thus, progressively higher Gd/Yb ratios (Fig. 5), coupled with identical La normalized concentrations (Fig. 4a), suggest an increase of influence of residual garnet in the mantle source, implying a deeper start of melting relative to those samples having lower Gd/Yb ratios.



Fig. 5. Gd/Yb vs. La/Yb chondrite-normalized concentrations for the studied basalts. The most magnesium-rich samples (black circles) show a good correlation between the two ratios and, coupled with the information obtained from figure 4a, could indicate a greater influence of mantle residual garnet in the melting source for samples having the highest (Gd/Yb)cn and (La/Yb)cn ratios.

Fig. 5. Diagrama de variação Gd/Yb vs. La/Yb (todas as concentrações normalizadas aos condritos) para os basaltos estudados. As amostras mais magnesianas (círculos negros) mostram uma boa correlação e, integrando a informação obtida na figura 4a, poderá indicar para as amostras com as maiores razões em (Gd/Yb)cn e (La/Yb)cn que a fusão parcial terá ocorrido sob efeito da granada residual no manto.

2.3. Crystal fractionation

In order to explain the chemical variability of PO-1 lavas, crystal fractionation modelling was carried out. Commonly, crystals are thought to be removed from their site of formation and hence the distribution of trace elements is not an equilibrium process. Thus, fractional crystallization is better described by the Rayleigh Law, instead of the equilibrium crystallization.

The modelling assumed sample 434/1 as the parental magma composition (a reasonable assumption based on the diagrams of figures 1 and 3, and considers plagioclase, olivine, and clinopyroxene, as the crystallizing phases in the proportion of 2:1:1. The mineral-liquid partition coefficients are from Rollinson (1993). The results obtained allowed to conclude that crystal fractionation of 5 to ~50% can explain most of the chemical variety in PO-1 basalts (Fig. 6a).

Additional support for these crystal fractionation modelling results were obtained by applying the same methodology to the REE group, through the comparison of theoretical chondrite-normalized values to those determined from the lavas, and identical values for the extent of crystal fractionation were obtained.

It is relevant to emphasise that selection of segregating assemblage has important effects on the fractionation modelling, particularly the absence or presence of clinopyroxene since this mineral has clearly higher mineral/liquid partition coefficients for the least incompatible elements, when compared to olivine or plagioclase (e.g. Rollinson, 1993; Blundy *et al.*, 1998). The covariation obtained from MgO *vs*. CaO/Al₂O₃ diagram (CaO/Al₂O₃ ratio is sensitive, in an opposite way, to both plagioclase fractionation (ratio increases) and clinopyroxene fractionation (ratio decreases); olivine fractionation has no effect on the ratio) clearly indicate the involvement of clinopyroxene as a fractionated mineral phase (Fig. 6b). This conclusion was supported by using the Petrolog software package (Danyushevsky, 2001), which is based on certain algorithms established through experimental data, providing theoretical magma differentiation throughout the calculation of the so called liquid-lines-of-descent.



Fig. 6. a) Plot representing the co-variation between Nb and Zr with superimposed theoretical lines representing the effects of variable degrees of crystal fractionation (C.F.) for the studied lavas; each cross represents an increment of 5% in C.F. To justify the elements relationship it is necessary to invoke variable C.F. percentages, from 5% to a maximum of 55%. b) Variation diagram between CaO/Al₂O₃ ratios and MgO.The liquid-lines of descent for fractional crystallization calculated following Danyushevsky (2001) are superimposed on the determined chemical data. The minerals chosen to belong to the fractionating assemblage are plagioclase, olivine and clinopyroxene (dotted line). However, to evaluate the effect of absence of clinopyroxene in the CaO/Al₂O₃ variation, the fractional crystallization process was modelled only considering the plagioclase + olivine as the fractionation minerals (segmented line). The circles represent the most primitive lavas derived by variable percentage of mantle melting.

Fig. 6. a) Diagrama representando a co-variação entre o Nb e o Zr para as lavas estudadas. A linha representa os resultados da modelação efectuada para a cristalização fraccionada (C.F.); cada cruz representa um incremento de 5% na C.F. Para justificar a relação obtida entre estes elementos (e outros pares de elementos não representados), é necessário invocar variáveis percentagens de C.F., de 5% até um máximo de 55%. b) Diagrama de variação entre as razões CaO/Al₂O₃ e o MgO. As linhas teóricas obtidas para a C.F. foram modeladas seguindo a metodologia de Danyushevsky (2001) e estão sobrepostas aos dados químicos determinados. Considerou-se que os minerais fraccionados foram a plagioclase, olivina e piroxena (linha a ponteado). Contudo, para avaliação da não fraccionação da clinopiroxena, o processo de C.F. foi modelado considerando somente a cristalização de plagioclase e olivina (linha segmentada). Os círculos representam as lavas mais primitivas geradas por variáveis graus de fusão mantélica.

The occurrence of clinopyroxene as an earlier crystallizing phase in these lavas is consistent with conclusions reached in studies of MORB from a number of other localities (e.g. Reynolds & Langmuir, 1997). The results obtained in this study are in agreement with the socalled "pyroxene paradox", which is observed in a number of studies (e.g. Batiza & Niu, 1992) and is a consequence of the dominance of modal plagioclase and the general absence of modal pyroxene phenocrysts in MORB lavas compositional evidence of with clinopyroxene crystallization. This paradox is attributed to the density contrast between clinopyroxene and the host magma coupled with the increasing olivine phase volume at decreasing pressure, and consequent resorption of clinopyroxene en route to the surface (e.g. le Roux et al., 2002). Thus, the observed modal mineralogy of a basalt does not necessarily reflect the cotectic proportions of the crystallizing phases and the qualitative presence of a phase is petrogenetically more significant (e.g. Stakes et al., 1984).

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