Geof. Int. Vol. 18: 4, 1979, pp. 385-394

EFFECTS OF LOW TEMPERATURE SEA-FLOOR WEATHERING ON THE RARE EARTH ELEMENTS OF THOLEIITIC BASALTS

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(Received June 1st., 1979)

RESUMEN

El presente trabajo se basa en resultados de elementos de tierras raras obtenidos de basaltos toleíticos provenientes de la boca del Golfo de California, México. Los basaltos fueron muestreados durante una operación de dragado a la latitud de 23° N.

Los elementos de tierras raras fueron obtenidos por el método instrumental de activación por neutrones (López *et al.*, 1978). Las muestras fueron tomadas entre la cresta de la Dorsal del Pacífico Este y la plataforma continental de la península de Baja California. Las edades asignadas a las muestras con base en datos de anomalías magnéticas y de la relación batimetría-edad del fondo oceánico son de 0, 1.7 y 3.5 millones de años. Los datos son empleados en este trabajo para evaluar el comportamiento de las tierras raras durante procesos de alteración a bajas temperaturas. Fue usado un procedimiento de normalización propuesto por Ludden y Thompson (1978) para datos de basaltos de la dorsal del Atlántico Medio (23° N). No obstante que el valor de normalización (esto es, la abundancia de Yb para basaltos sin alteración) puede no ser válido para los basaltos de la Dorsal del Pacífico Este (23° N), los resultados obtenidos son consistentes y reflejan los efectos de alteración. Dichos resultados están de acuerdo con el modelo propuesto por Ludden y Thompson. Las muestras reflejan un enriquecimiento progresivo de las tierras raras ligeras (La a Sm) con la alteración (edad). Por otro lado, las diferencias observadas con respecto a los resultados anteriores indican que las tierras raras no se comportan de igual forma en todos los ambientes de alteración. En particular, el elemento Ce muestra anomalías positivas y negativas, contrario a lo esperado del modelo propuesto que predice anomalías negativas. El agua de mar tiene una anomalía negativa, de aquí que este comportamiento puede ser interpretado en términos de la abundancia de Ce en el agua de mar o bien su fraccionamiento del agua de mar.

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ABSTRACT

We have recently presented (López *et al.*,1978) rare earth element (REE) data for tholeiitic basalts sampled during a dredging transect at 23° N in the mouth of the Gulf of California, Mexico. The samples are distributed between the East Pacific rise (EPR) crest and the Baja California continental slope and covering a short time span of 0 to 3.5 million years. These data have here been used to evaluate the behaviour of the REE during low-temperature weathering processes. In doing this, a normalization procedure proposed by Ludden and Thompson (1978) for the Mid Atlantic ridge at 23° N is used. Although the normalizing value may not be a strictly valid value for the EPR, the results do agree with the low-temperature weathering model of Ludden and Thompson. The samples show an increasing enrichment of light-REE (La-Sm) with weathering (increasing age). The differences however observed between the two sets of results indicate that the REE do not behave exactly in the same way in all weathering environments. In particular cerium behaves inconsistently showing negative and positive anomalies. Seawater displays a cerium depletion, thus this behaviour may reflect its seawater abundance or its fractionation from seawater.

INTRODUCTION

The study of the rare earth elements (REE) when considered relative to chondritic abundances has been considered as a very valuable diagnostic tool in a variety of investigations. The generally accepted proposition that the REE show little migration during secondary alterations (e.g. Frey *et al.*, 1968; Philpotts *et al.*, 1969 ; Schilling, 1973, 1975; Herrmann *et al.*, 1974; Kempe and Schilling, 1974; Condie, 1976; García, 1978) has recently been challenged by Ludden and Thompson (1978), who have demonstrated that a significant uptake of the light REE (La-Sm) occurs during weathering processes at low temperatures of sea-floor tholeiitic basalt. The samples studied were dredged basalts collected from the Mid-Atlantic ridge at 23° N. The ages of these samples ranged from 0 to 5 Myr on the basis of the magnetic anomaly pattern. From their results, geochemical and petrological inferences based on the stability of REE in tholeiitic basalts should be modified. Thus, it is pertinent to see if Ludden and Thompson's findings are present in other submarine basalts.

LOW-TEMPERATURE SEA-FLOOR WEATHERING OF THOLEIITIC BASALTS

Ludden and Thompson (1978) found that the REE patterns of basalts show a light-REE enrichment (La-Sm) and a relatively constant heavy REE pattern during low-temperature submarine weathering. These authors explained their findings by assuming that the REE patterns are the reflection of the REE abundance in seawater. The proposed control of the fractionation of light-REE from seawater during weathering is the hydrolysis potential of the REE. Goldberg *et al.* (1963) and

Hogdahl *et al.* (1968) have shown that the chondrite normalized REE pattern of seawater displays a decreasing enrichment with atomic number for the light-REE and a relatively constant heavy REE pattern. In addition, Glasby (1972) has shown that the solubility product for the trivalent REE hydroxides decreases strongly from La to Sm but is relatively constant from Eu to Lu. The chondrite normalized pattern of seawater also displays a depletion in Ce which has been attributed by Ludden and Thompson as the result of oxidation of Ce to the tetravalent state and its later fractionation from seawater (Glasby, 1972; Piper, 1974).

In summary, one may expect that during low-temperature weathering of tholeiitic basalt the chondrite normalized REE pattern shows a light-REE enrichment with less enrichment in Ce and a relatively constant heavy-REE pattern.

DATA ANALYSIS AND DISCUSSION

We have recently analyzed (López *et al.*, 1978) three tholeiitic basalts dredged from the East Pacific rise (EPR) at the mouth of the Gulf of California (∿ 23° N) between the Rivera and Tamayo fracture zones. The samples are distributed between the rise crest and the Baja California continental slope (Figure 1) and their ages have here been assigned on their position relative to magnetic anomalies and bathymetry-age relationships (Flores and González, 1977; Urrutia Fucugauchi, 1978). The samples belong to a different tectonic setting to those of Ludden and Thompson since they are from a fast spreading system (⩾ 3 cm/yr) while the Mid-Atlantic ridge is a slow spreading one (⩽ 3 cm/yr). The corresponding REE data for the EPR basalts are reproduced in Table 1. To give an idea of the instrumental differences between this analysis and that carried out by Ludden and Thompson, in Table 1 are also included the results from the U.S.G.S. standard rock sample BCR-1 which was analyzed in both studies with respect to the Flanagan (1973) recommended values.

For comparison purposes, Ludden and Thompson used a normalization procedure which consists of normalizing the REE abundances of the weathered samples to the average Yb value of the unweathered ones. The chondrite normalized (Masuda *et al.*, 1973; Masuda, 1975) REE patterns of the EPR samples show a general agreement with the Ludden and Thompson proposed pattern. The REE data display an increasing enrichment for the light-REE and a relatively constant heavy-REE pattern as the samples increase their distance from the rise crest. To proceed further, the Yb value used by Ludden and Thompson (1978) in their normalization procedure was used for the EPR samples. Though this value may not reflect the Yb abundance of the fresh basalts of this EPR region, the conclusions reached using this normalizing value are identical to the ones we will have reached using the Yb content of the sample DH-01 from the EPR as the normalizing value. The results of such a normalization procedure are shown in Figure 2. The shaded region represents the range in abundance for the fresh basalts at the Mid-Atlantic ridge (23^{o} N). A general agreement can be noted with the EPR samples showing an increasing enrichment of light-REE with weathering (increasing age of the ocean crust and distance from the rise crest). The extent of weathering was discussed in López *et al.* (1978) and may be reflected by the H_2O^+ and the LOI ($H_2O^+ + CO_2$) variations (Philpotts *et al.*, 1969; Hart, 1969). Another evidence is given by the Fe_2O_3/FeO ratio which increases with alteration (see Table 1). In particular the agreement shown by the sample DH-01 with the results from the Mid-Atlantic ridge strongly justifies using the normalization procedure. However, the O Myr (DH-01) sample shows a Ce enrichment and a depletion in Eu relative to the fresh Mid-Atlantic ridge basalt. Although this sample was collected from the rise crest (Figure 1) it showed distinct evidence of alteration (López *et al.*, 1978) and this may explain the apparent discrepancy. According to the model introduced by Ludden and Thompson the seawater displays a Ce depletion which is reflected in the weathering effects, but the Ce anomaly for this sample DH-01 is reversed (Figure 2). The 1.7 Myr (DH-12) sample shows an enrichment in La, Nd and Sm, and a Cs depletion in agreement with the low-temperature weathering model. It also shows a well marked depletion in Eu. Finally, the 3.5 Myr (DH-08) sample also shows an enrichment in light REE. The main differences between these results and those of Ludden and Thompson are a Ce enrichment in the 0 Myr sample and a depletion in Eu in the 0 Myr and 1.7 Myr samples. The negative and positive Ce anomalies may be explained in terms of the Ce abundance in seawater or its fractionation from seawater. Additional analysis from the zone of the Mid Atlantic ridge using samples from 0 Myr to 57 Myr show positive and negative Ce anomalies (Ludden, personal written communication, 1978). Thus, Ce behaves inconsistently, and may be either depleted or enriched relative to the other light REE. The depletion in Eu may reflect removal of feldspar in predominantly reducing conditions, resulting in a high Eu^{+2}/Eu^{+3} ratio, by a process of fractional cristallization (feldspar accepts Eu^{+2}).

It is generally difficult to assess when recovered rocks were *in situ* and their association and relative abundance with the other rocks on a given area of ocean floor. Thus, results from dredged rocks may not be directly applicable to the rest of the ocean crust. In addition, dredged rocks are from the shallower part of the ocean crust and have presumably been exposed to seawater alterations since their formation. In contrast, for deeper rocks seawater circulation may cease or be severely restricted soon after their formation. Therefore, there is no reason to assume that data from dredged samples may be directly applicable to drilled basalts, if only because their respective environments must considerably differ. Thus, the fact that results from drilled basalts from the DSDP which do not show enriched light-REE pattern in the palagonitized samples (e.g. Staundigel *et al.*, 1978; Hart and Staundigel, 1978) support that the effects here discussed are related to the environment of alteration.

In summary, I feel that the data of the EPR samples agree with the results presented by Ludden and Thompson (1978), though only three analysis are not considered statistically significant, and further support their model and that, inferences based on assumed REE immobility for weathered tholeiitic basalts must be treated with caution. The differences observed between the two sets of results suggest, in consonance with other recent studies (e.g. Thompson, 1973; Frey *et al.*, 1974; Hellman and Henderson, 1977; Hellman *et al.*, 1977; Hart and Staundigel, 1978), that the REE may not behave exactly in the same way in all weathering environments. Therefore, much more data are required before a general model can be put forth.

ACKNOWLEDGMENTS

I wish to thank Drs. John N. Ludden (Woods Hole Oceanographic Institute, U.S.A. and Université de Montreal, Canada) and Don H. Tarling (University of Newcastle upon Tyne, England) for their comments and criticisms in critically reviewing this manuscript. I would also like to thank the two anonymous reviewers for their helpful reviews.

TABLE 1. REE analysis (in ppm) of basalts dredged from the mouth of the Gulf of California, Mexico.

ELEMENT	DH-01	DH-12	DH-08	BCR-1	
AGE	0 Myr	1.7 Myr	3.5 Myr	diff. EPR samples (%) †	diff. Mid-Atl. samples (%) †
La	2.7	2.9	4.7	-3.85	-5.38
Ce	11.6	8.3	16.4	-5.38	-0.56
Nd	7.8	11.8	13.4	17.24	-8.28
Sm	4.1	3.9	4.0	3.03	-7.58
Eu	1.05	1.0	1.45	4.12	-3.09
Gd*	5.0	4.0	5.8	-9.09	-
Tb	0.84	0.75	1.02	12.0	10.0
Ho**	-	-	-	-	-1.67
Tm*	0.48	0.58	0.44	6.67	-
Yb	3.07	2.59	2.65	-1.79	-1.19
Lu	0.54	0.46	0.42	1.82	0.0
Fe_2O_3/FeO	0.37	0.77	1.70		

† {(element abundance - Flanagan value)/ Flanagan value} x 100 %

* element not determined in Ref. 4

** element not determined in Ref. 5

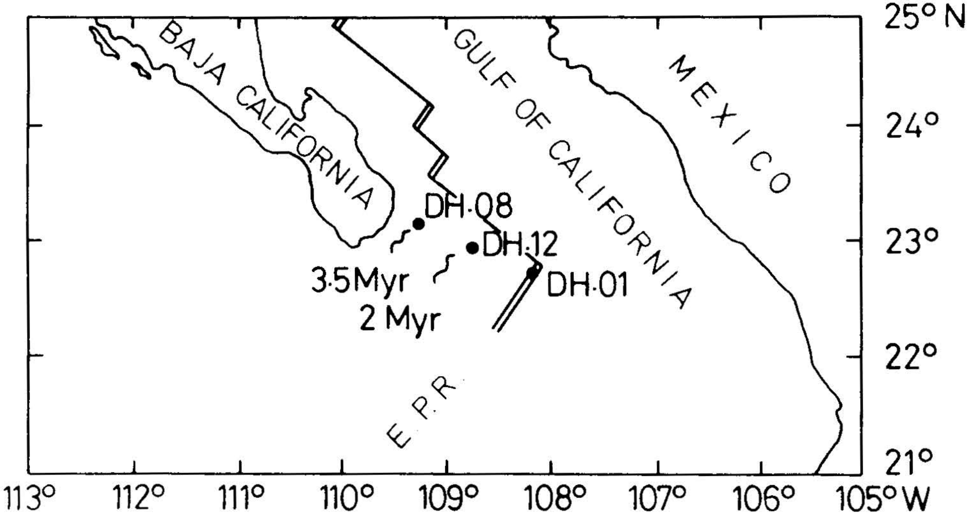

Fig. 1. Location of the EPR samples.

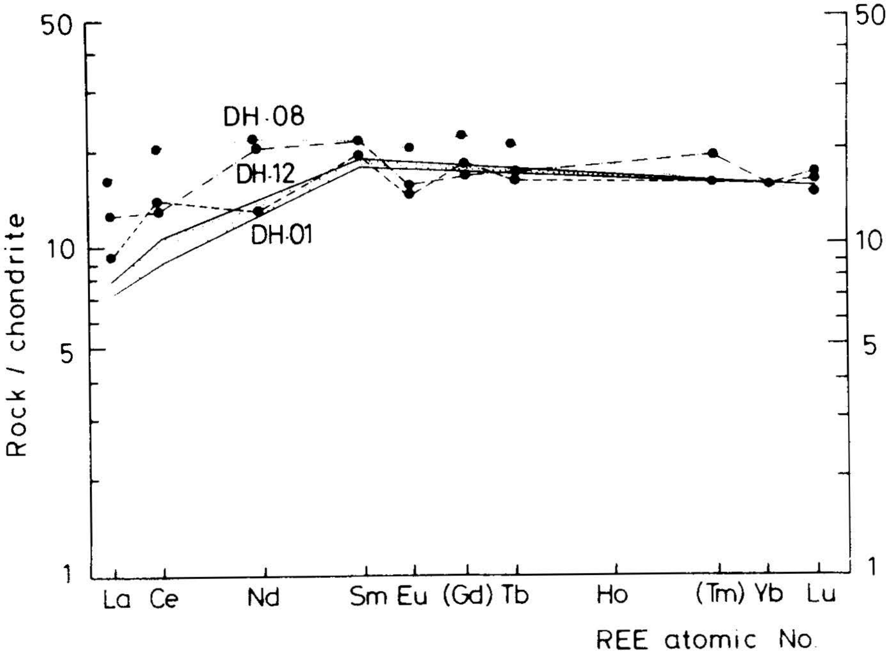

Fig. 2. Chondrite normalized REE profiles for the EPR samples after normalization to an average Yb value for fresh basalts from the Mid-Atlantic ridge at 23° N. The shaded region represents the range in abundance for the basalts of the Mid-Atlantic ridge axis. Gd and Tm were not determined for the Mid-Atlantic samples, and Ho was not determined for the EPR samples.

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