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Rare Earth Element Concentrations in Mafics from the Kızıl Dağ Ophiolite (Hatay, Turkey)

by Delaloye, M.¹), Piskin, Ö.²), Voldet, P.¹), Vuagnat, M.¹) and Wagner, J.-J.¹)

Abstract

Abundances of rare earth elements (REE) from the mafic sequence of the Kızıl Dagh – Hatay ophiolite have been measured by neutron activation technique for short lived isotopes. The results for twelve samples from the gabbroic part show a general REE pattern with a depletion in the light REE (LREE) indicating that these rocks were derived from a uniform LREE depleted asthenosphere source (SCHILLING, 1975) at a spreading zone. The REE abundances vary by a factor 6 to 10 between the cumulate gabbros from the ultramafic – transition zone and the high level microgabbros from screens in the dyke complex.

Özet

Kızıl Dagh – Hatay ofiyolitini teşkil eden mafik kayaçlardaki lantanit elementlerin miktarları nötron aktivasyon metodu ve kısa periyodlu izotopların ölçümüyle tayin edildi. Gabrolara ait 12 numuneden elde edilen neticeler hafif lantanitler için genel bir azalma göstermektedir. Bu da, bu kayaçların kaynaginın hafif lantanitler için homojen bir azalmaya uğraniş genişleme otanındaki bir astenosfer oldušunu gösterir (SCHILLING, 1975). Filon komplexinde ki ektanlara ait üst seviye mikrogabroları, ultramafik-mafik geçişme sahasındaki gabrolara kiysla 6 ile 10 defa daha fazla miktarda lantanit elementleri ihtiva elmektedirler.

1. INTRODUCTION

Ophiolitic massifs are a major center of interest because they are thought to be pieces of an ancient oceanic crust formed at a spreading axis (GASS, 1968, DEWEY et al., 1973, MOORES et al., 1974). However, it is very difficult to determine if the ophiolites were part of a mid-ocean ridge or part of a back arc basin. Although we cannot actually decide from the geochemistry of the REE to which paleoenvironment the Kızıl Dagh ophiolite belongs we can use the REE

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concentrations to elucidate the processes related to the formation of magma from the upper mantle. This study may help to characterize ophiolites from different settings.

A systematic investigation of the REE of the different members of the Kızıl . Dagh ophiolite is in progress and in the present paper we discuss our data on the gabbroic member.

2. GEOLOGICAL SETTING OF THE KIZIL DAĞ

The K121l Dagh ophiolite massif represents the S-W end of the Amanos Range close to the border between Turkey and Syria. The massif is cut abruptly by a major fault running N-S which forms the shoreline. Rising to 1800 m above sea level, a very impressive outcrop is visible along the coast. The K121l Dagh was first mapped by DUBERTRET (1953) and described as a single huge submarine flow of Upper-Cretaceous age that has differentiated by gravity, with transition from fine grained basaltic rocks to coarse-grained ultramafics. The massif was later on interpreted as an ocean floor lithosphere by VUAGNAT et al. (1967). They recognized particularly the presence of a sheeted complex of dykes with chilled edges against screens of gabbros. Further studies have been done by Çoğulu (1973, 1974, 1976) and PARROT (1973).

The ophiolite suite can be characterized as follows:

- a) ultramafic tectonites (harzburgites and dunites) form the center of the massif,
- b) ultramafic cumulates formed by fractional crystallization of a magma produced by partial melt of the mantle (JACKSON, 1971). They outcrop mainly towards the SE edge of the massif,
- c) mafic rocks like olivine gabbros or amphibole gabbros showing a variety of banding and flow structures,
- d) a five kilometers wide sheeted complex formed of dolerites dykes with few gabbros screens,
- e) pillow lavas of basaltic composition outcrop to the NE.

The contacts between these members have often a tectonic character. One may also recall that a previous paleomagnetic study (WAGNER et al., 1976) did not show any magnetic field reversals; measured ages (DELALOYE et al., 1977) show that the Kızıl Dagh ophiolite seems to have acquired its sea floor magnetization during a normal polarity geomagnetic period.

3. ANALYTICAL METHODS

The determination of REE concentrations was made by neutron activation followed by high-resolution X-Ray spectrometry or γ -spectrometry.

For a number of years neutron activation analysis has been used for the determination of rare-earth elements in rocks. We propose a method for the simultaneous determination of eight to ten REE in the mafics of an ophiolite (gabbros, dolerites, basalts). Before neutron activation, the RE elements **m**ust be separated from the other elements present in rocks so as to obtain the same matrix for rocks and standards for the measurements of activity. This separation is done by gravimetry and column chromatography; the procedure is described by VOLDET and HAERDI (1976). The standards were prepared by precipitation of the oxalates of mixtures of RE elements in proportions suitable for mafic rocks.

Samples and standards were first irradiated for 30 min. in the AGN-201-P reactor of Geneva University at a thermal neutron flux of 10⁹n.cm⁻².s⁻¹ and Eu and Dy were determined. Then, the same samples and standards were irradiated for 10 hours in the Diorit reactor of the Swiss Federal Institute for Reactor Research, Würenlingen at a thermal neutron flux of about 2,5.10¹²n.cm⁻².s¹ and the following REE were determined;

 b) by γ-spectrometry (crystal Ge[Li]): Gd(¹⁶¹Tb) (t¹/₂, 7.2 d), ¹⁷⁷Lu (t¹/₂, 6.75 d), ¹⁴³Ce (t¹/₂, 33 h) and ¹⁴⁰La (t¹/₂, 40.3 h).

These activities are measured after a cooling time of about 36, 60 and 110 hours. Each sample is counted for 500 s with the Ge detector and 60 s with the Ge(Li) detector. For X-Ray spectrometry, the equipment used is described in our work (Loc. cit.), and for γ -spectrometry the following equipment was used:

Ge(Li) detector (Seforad, 50 cm^3), preamplifier Seforad SR-100, amplifier Ortec 472 and a 4096 channel Zoomax SEIN analyzer (VOLDET and HAERDI, 1978). The precision (of the order of 5 to 20%) is limited principally by the accuracy of the measurement method. No interference of other elements was observed; this confirms the validity of the separation method.

The method has been tested on several standard rocks; the following results are obtained for the U.S.G.S. standard rock BCR-1:

| Element La | Ce | Sm | Eu | Gd | Dy | Ho | Lu | • |
|---------------|------|-----|------|-----|------|-----|-----|---|
| Value in 23.4 | 50.9 | 6.2 | 1.90 | 7.2 | 6.34 | 1.6 | 2.4 | |

a) by high-resolution X-Ray spectrometry (crystal Ge):
^{152m}Eu (t¹/₂, 9.3 h), ¹⁵³Sm (t¹/₂, 46.5 h), ¹⁶⁶Ho (t¹/₂, 1.12 d), ¹⁷⁷Lu (t¹/₂, 6.75 d), ¹⁶⁶Yb (t¹/₂, 30.6 d),
¹⁴⁷Nd (t¹/₂, 11.1 d) and ¹⁴³Ce (t¹/₂, 33 h);

The values from La to Ho are in agreement with those published by several authors (MENZIES, 1976). One has to be careful with the value of Lu which in our case is 2.4 ppm and normally is given as around 0.6 ppm.

4. RESULTS AND DISCUSSION

Several Eastern Mediterranean ophiolites such as the Troodos, Pindos and Othris have been studied for their REE concentrations (e.g. KAY et al., 1976, MENZIES, 1976). They exhibit a general REE pattern which can be summarized from the Troodos ophiolite:

- a) All rocks have the same trend showing a depletion in light REE (LREE).
- b) The concentration of REE increases by roughly a factor of 50 from the gabbros to the pillow lavas.

The general trend indicate that these rocks were derived from a uniform LREE depleted asthenosphere.

As our gabbros are from different type we have analyzed some specific samples such as cumulate gabbros, high level gabbros and a dyke of pegmatitic gabbro, the results are given in Table 1. All these data have been normalized with respect to the REE distribution for chondrites given by NAKAMURA (1974); the resulting ratios are presented in Table 2. Looking at those results one notices that with the exception of the La ratio for samples M44 and M69, all our gabbros have REE abundances higher than the chondrites in respect with some of the Troodos gabbros for example (KAY et al., 1976) who have abundances ratios lower than one.

| Samples nb. | M44 | M45 | M48 | M50 | M52 | M66 | M68 | M69 | M70B | M81 | M85 | M103 |
|-------------|------|--------|------|------|------|------|------|------|------|------|------|------|
| La | 0,2 | 0,7 | 3,2 | 0,5 | n.đ. | 0,7 | 1,2 | 0,2 | 0,7 | 0,8 | 2,1 | 1,0 |
| Ce | n.d. | < 15 * | < 15 | < 15 | < 15 | < 15 | < 15 | < 15 | < 15 | < 15 | < 15 | < 15 |
| Sm | 0,5 | 0,7 | 1,7 | 0,7 | 0,7 | 0,5 | 0,9 | 0,3 | 0,7 | 0,9 | 1,7 | 0,9 |
| Eu | 0,2 | 0,3 | 1,5 | 0,4 | 0,2 | 0,5 | 0,7 | 0,2 | 0,5 | 0,5 | 1,0 | 0,6 |
| Dy | 1,0 | 1,5 | 8,2 | 1,8 | 1,5 | 2,6 | 3,3 | 1,0 | 2,7 | 1,8 | 5,5 | 3,1 |
| Но | 0,5 | 0,5 | 0,3 | 0,6 | 0,5 | 0,3 | 0,6 | 0,1 | 0,7 | 0,8 | 1,2 | 1,0 |
| Yb | n.d. | 1,2 | 2,0 | 3,2 | 1,1 | 1,2 | 1,4 | 0,4 | 3,2 | 3,0 | 3,3 | 4,4 |
| Lu | 0,3 | 0,1 | n.d. | 0,3 | 0,1 | 0,2 | 0,2 | 0,1 | 0,3 | 0,4 | 0,5 | 0,6 |

Table 1. REE abundances (ppm) of different kinds of gabbros

* for Ce values below the sensitivity of our method is quoted <15.

| | a | M44 | M45 | M48 | M50 | M52 | M66 | M68 | M69 | M70B | M81 | M85 | M103 |
|----|---|-------|-------|--------|--------|-------|-------|-------|-------|--------|--------|--------|--------|
| 57 | La (0.329) | 0.606 | 2.128 | 9.726 | 1.520 | - | 2.128 | 3.647 | 0.608 | 2.128 | 2.432 | 6.383 | 3.039 |
| 58 | Ce (0.865) | - | - | - | - | - | - | - | | - | - | - | - |
| 62 | Sm (0.203) | 2.463 | 3.448 | 8.374 | 3.448 | 3,448 | 2.463 | 4.433 | 1.478 | 3.448 | 4.433 | 8.374 | 4.433 |
| 63 | Eu (0.070) | 2.597 | 3.896 | 19.480 | 5.945 | 2.597 | 6.493 | 9.091 | 2.597 | 6.493 | 6.493 | 12,987 | 7.792 |
| 66 | Dy (0.343) | 2.915 | 4.373 | 23.906 | 5.248 | 4.373 | 7.580 | 9.621 | 2.915 | 7.872 | 5.248 | 16.035 | 9.038 |
| 67 | Ho (0.070) ^b | 7.142 | 7.149 | 4.885 | 8.571 | 7.142 | 4.285 | 8.571 | 1.428 | 10.000 | 11.428 | 17.142 | 14.285 |
| 70 | Yb (0.220) | - 1 | 5.454 | 9.091 | 14.545 | 5.000 | 5.454 | 6.364 | 1.818 | 9.999 | 13.636 | 14.999 | 20.000 |
| 71 | Lu (0.034) | 8.823 | 2.941 | - | 8.823 | 2.941 | 5.882 | 5.882 | 2.941 | 8.823 | 11.764 | 14.706 | 17.647 |
| | a. Chondrite values By Nakamura (1974) in ppm | | | | | | | | | | | | |

Table 2. Normalized REE ratios

b. Value extrapolated from average chondrite plot.

The ratios of four typical gabbros are plotted on a logarythmic scale against REE in increasing atomic number in abcissa (Fig. 1). From this figure it can be seen that the REE patterns are more or less parallel to each other but large differences in concentrations exit. All samples exhibit a depletion in LREE and most of them have a positive Europium anomaly with respect to the neighbouring elements (in our case Sm and Dy). This anomaly is generally related to the cumulate plagioclase.

A crude analysis of the data shows that the high level gabbros sampled in screens in the sheeted complex (e.g. microgabbro M85) have the same REE



REE VARIATION PROFILES OF THE KIZIL DAG GABBROS

Fig. 1 Relative rare earth element patterns of four typical gabbros.

abundances as the dykes from the complex; similar observations have been made by KAY and SENECHAL (1976) in the Troodos, they concluded "... Thus the gabbros in the plutonic complex appear to be derived by crystal sorting from magmas with the same REE pattern as the dykes and lavas".

It is also very interesting to compare the REE behaviour in the cumulate transition zone where one finds interbedding of cumulate gabbro (sample M50) and cumulate peridotite (sample M52, wehrlite). In the latter the REE abundances are lower as expected from ultra-mafic material; La is not detected, Eu exhibits a negative anomaly. The only common point for both samples is the same ratio of Sm.

Another interesting point is that the pegmatitic gabbro sample M81 coming from a dyke in the peridotite has the same pattern with similar abundances as the cumulate gabbro M50.

Finally the olivine gabbro-norite M69 with olivine and two pyroxenes (opx, cpx) has the lowest general trend in agreement with the REE partition rules giving the relative REE content of the main minerals

hbl > cpx > pl > opx > ol

CONCLUSION

As our REE results on gabbros represent only a step of our REE investigation of the Hatay ophiolite, it is difficult to draw a definite conclusion. Nevertheless one may emphasize that the cumulate and non cumulate gabbros are related to each other by an evolutionary process. It has been shown that the concentrations are varying from 0.6 to $8.8 \times$ chondrites for a cumulate gabbro to 6.4 to 14.7 for a microgabbro of the top of the plutonic system.

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