# Instrumental neutron activation analysis for rare earth elements in dolerite dykes of Kuantan area, Peninsular Malaysia

G. Sita Ram[1], K.R. Chakraborty[2] and Sharifah Barlian Aidid[3]

**Abstract:** The REE abundances in five dolerite dykes (olivine tholeiite to quartz tholeiite) from Kuantan have been determined by instrumental (non-destructive) neutron activation analysis using reactor irradiation and high-resolution gamma-ray spectroscopy. The analytical procedures followed in this work are discussed.

A total of nine rare earths (La, Ce, Nd, Sm, Eu, Gd, Tb, Yb and Lu) have been measured. The dykes show fractionated REE patterns with chondrite-normalised values ranging from about 34 to 105 for La and from about 8 to 11 for Yb. The concentrations of individual elements as well as the $\Sigma$REE increase systematically with increasing differentiation. The more evolved rocks show positive Eu anomaly. The variations in REE abundances are compatible with a crystal fractionation (clinopyroxene and olivine) model of evolution interpreted from petrography and major element chemistry.

## INTRODUCTION

Instrumental (non-destructive) neutron activation analysis (INAA) using reactor irradiation and high-resolution gamma-ray spectormetry has only recently been started in Malaysia (Sita Ram, 1979). Since no nuclear reactor is yet locally available, the samples have to be sent abroad for irradiation and flown back after a certain period of waiting time. This allows for analysis of relatively long-lived radioactive product nuclides only. At present it is possible to determine about twenty-five trace elements including rare earth elements (REE) and three major elements (Fe, Na and K) in silicate rock samples. The availability of this analytical technique provides the opportunity for systematic studies of REE geochemistry locally.

In the present work we report, for the first time, the abundances of nine rare earth elements (La, Ce, Nd, Sm, Eu, Gd, Tb, Yb and Lu) in five dolerite dyke samples from the Kuantan area. The main objective of this short communication is to outline the procedures followed by us for INAA and to comment briefly on the REE distribution patterns of the dykes. Detailed discussion on the petrogenesis of the dolerites based on REE is beyond the scope of this article. Petrogenetic aspects will be considered in a separate paper along with other trace and major element data.

## GEOLOGICAL BACKGROUND

Dolerite dykes, of probable Late Cretaceous–early Tertiary age, occur in and around Kuantan, Pahang, as thin tabular sheets intruding into Late Permian granite (ca. 250 Ma, Bignell and Snelling, 1977). These dykes have previously been described by

[1]. Nuclear Science Unit, Universiti Kebangsaan Malaysia, Kuala Lumpur.
[2]. Department of Geology, University of Malaya, Kuala Lumpur.
[3]. Department of Physics, Universiti Kebangsaan Malaysia, Kuala Lumpur.

Fitch (1951) and Hanif (1975). The field relations of the dykes and other relevant information can be found in these works. From detailed petrographic and major element geochemical studies, it has been established that the dykes range in composition from olivine tholeiite to quartz tholeiite and bear affinity to the tholeiites of continental setting (K.R. Chakraborty, unpublished work). The bulk compositions and the major element variation patterns of the dolerites point to their evolution through crystallization differentiation controlled mainly by fractionation of clinopyroxene and olivine in the early stages. The REE data presented in this paper would be valuable for further evaluation and testing of this evolutionary model.

## SAMPLE SELECTION

A number of dykes have previously been analysed for major elements out of which five samples have been chosen for REE determination. The samples are selected to cover all the petrographic types from olivine tholeiite to quartz tholeiite, and to represent rocks of various stages of evolution using $FeO^*/(FeO^* + MgO)$ as a qualitative fractionation index ($FeO^*$ = total iron as FeO). The more evolved rocks have higher $FeO^*/(FeO^* + MgO)$. The dykes are altered to varying degrees and care has been taken to select the least altered rocks as far as possible.

## EXPERIMENTAL DETAILS

**Sample Preparation and Irradiation:** The five dyke samples and several USGS standard rocks (BCR-1, AGV-1, G-2 and others) in fine and dry powder form were accurately weighed (about 100 mg each) into clean polyethelene bags ($20 \times 25$ mm$^2$) and heat sealed. Each sample bag was then sealed in another polyethelene bag as a safety precaution.

The samples and standards were stacked together[4]. Four aliquots of BCR-1 (100 mg each) were placed equidistantly along the length of the stack (one at each end and two in the middle section) with a view to correct for the neutron flux gradient during irradiation. The samples were irradiated at the Bhabha Atomic Research Centre, Trombay, India, at a thermal neutron flux of $1.2 \times 10^{12}$ neutrons cm$^{-1}$ s$^{-1}$ for a continuous period of 12 hours and flown back to Kuala Lumpur (after a waiting time of 3 days) for subsequent analysis in the Nuclear Science Laboratory of Universiti Kebangsaan Malaysia.

**Measurement of the Activities:** The radioisotopes (gamma emitters only) of the rare earth elements that could be measured after the arrival of the irradiated samples in Kuala Lumpur are given in Table 1. The relevant nuclear data used in calculations are also given in the same table.

The high-resolution gamma-ray spectrometer used for the measurement of the activities has a 84.5 cm$^3$ Ge(Li)-detector and a 4096 channel analyzer as its major components. Details of this spectrometer and its use in INAA are given elsewhere (Sita Ram and Gangadharam, 1978).

---

[4]. The length of the stack was 54 mm. The stack contained 12 other Kuantan basalts, 17 tektites and 15 USGS rock standards. Except for the USGS standard BCR-1, no sample is duplicated. The analyses of the samples other than the dykes will be presented later.

After a decay time of 5 days (beginning from the end of irradiation period), a first set of measurements was carried out to determine all radionuclides with half-lives $\leqslant 7$ days. Each sample was measured for 2000 s. From these measurements the concentrations of La, Sm, Yb and Lu were determined. After a decay period of 3 weeks (by which time nuclides with low half-lives practically vanish) a second set of measurements was carried out to determine longer lived radionuclides. Each sample was measured for a period of 4000 s. From this set the concentrations of Ce, Nd, Eu and Tb were determined. After a decay time of about 80 days a third set of measurements was carried out to determine Gd and Tm. In this set each sample was measured for a period of 10,000 s.

Each radionuclide in all the samples was measured at least twice in order to reduce the counting errors. Each nuclide in BCR-1, which was also used as a comparison standard, was measured at least eight times in order to improve the precision of the final result. The activities in all the samples were corrected for neutron flux gradient along the length of the stack by measuring the activity of $^{59}$Fe radionuclide (half-life 45 d, gamma-ray energies 1099.2 and 1291.6 keV) in the four aliquots of BCR-1.

Gamma-ray peak intensities (also known as peak areas) were evaluated either manually or by automatic analyzer integration of suitable manually selected spectral regions of interest covering the peaks. The teletype output integrals were then processed by a programmable HP-97 calculator. The elemental concentrations were determined by comparing the normalised peak intensities of the relevant radionuclides in the sample and in the standard BCR-1.

Gamma-ray peaks used in calculations (Table 1) were selected taking into consideration the spectrometer efficiency, absolute intensities of spectral lines and spectral interferences. A detailed discussion of the problems involved is presented elsewhere (Sita Ram, 1979). Among the REE, only $^{141}$Ce, $^{175}$Yb and $^{170}$Tm suffer from spectral interferences. The 145.4 keV peak of $^{141}$Ce is corrected for interference

**TABLE 1.**

NUCLEAR DATA* USED FOR THE DETERMINATION OF REE

| Element | Isotope Measured | Half-life | Gamma-ray Energies (keV) |
|---|---|---|---|
| La | $^{140}$La | 1.68 d | 328.8, 487.1, 815.7, 1596.5 |
| Ce | $^{141}$Ce | 32.5 d | 145.4 |
| Nd | $^{147}$Nd | 11.1 d | 91.4, 531.0 |
| Sm | $^{153}$Sm | 1.94 d | 103.2 |
| Eu | $^{152}$Eu | 12.2 a | 121.8, 244.6, 778.6, 1086.0, 1407.5 |
| Gd | $^{153}$Gd | 242 d | 103.2 |
| Tb | $^{160}$Tb | 72 d | 897.4, 1177.9 |
| Ho | $^{166}$Ho | 1.12 d | 80.6 |
| Tm | $^{170}$Tm | 130 d | 84.3 |
| Yb | $^{175}$Yb | 4.19 d | 396.3 |
| Lu | $^{177}$Lu | 6.75 d | 208.4 |

*Bowman and MacMurdo (1974); Carder, Mac Mahon and Egan (1978)

from the 142.5 keV peak of [59]Fe. The 396.3 keV peak of [175]Yb is corrected for interference from the 398.2 keV peak of [233]Pa. The 84.3 keV peak of [170]Tm suffers strong interferences from [182]Ta (at 84.7 keV), [233]Pa (at 86.6 keV) and [160]Tb (at 86.8 keV). This problem is still under investigation. The 80.6 keV peak of [166]Ho could not be measured consistently in all samples due to its low half-life, and is therefore not reported here.

It should be mentioned that elements other than the rare earths were also measured simultaneously in all the samples during the course of this analytical work. These results will be presented at a later stage.

**Accuracy and Reliability:** In order to check the accuracy and reliability of our analyses, we have determined the REE concentrations in two \USGS standards, AGV-1 and G-2, treated as unknowns. Our results and the literature values are given in Table 2. The errors indicated in our results are counting errors only (one standard deviation). It may be seen from Table 2 that our data agree very well with the published values of these two standards. It is apparent therefore that by following our procedures quite accurate data can be obtained from a single analysis of a sample.

## RESULTS AND DISCUSSION

The REE concentrations of the five analysed dykes are presented in Table 3 and the chondrite-normalised (Haskin *et al.*, 1971) REE distribution patterns are shown in Fig. 1. As can be seen from Fig. 1, all the analysed dykes are enriched in REE relative to the chondrites. The sample/chondrite ratios for La vary from 34 to 105 and for Yb

**TABLE 2.**

CONCENTRATIONS (in ppm) OF REE IN USGS STANDARD ROCKS AGV-1 AND G-2

| Element | BCR-1* | USGS Standard AGV-1 | | | USGS Standard G-2 | | |
|---------|--------|-----------|--------|------|-----------|--------|------|
| | | This Work | Lit.** | PAB+ | This Work | Lit.** | PAB+ |
| La | 27 | 37.6 ±0.8 | 44.7 | 39 | 92.1 ±1.6 | 93.3 | 91 |
| Ce | 54.3 | 64.6 ±1.4 | 66.4 | 68 | 164 ±2 | 151 | 157 |
| Nd | 30.0 | 37.0 ±1.1 | 45.8 | 32 | 58.8 ±2.0 | 49.5 | 54 |
| Sm | 7.0 | 5.92 ±0.06 | 6.04 | 6.1 | 7.2 ±0.3 | 7.88 | 7.6 |
| Eu | 1.95 | 1.54 ±0.03 | 1.65 | 1.49 | 1.34 ±0.02 | 1.29 | 1.25 |
| Tb | 1.10 | 0.65 ±0.13 | 0.725 | 0.73 | 0.50 ±0.04 | 0.499 | 0.51 |
| Yb | 3.50 | 1.54 ±0.45 | 1.62 | 1.7 | 0.85 ±0.08 | 0.82 | 0.7 |
| Lu | 0.52 | 0.300 ±0.015 | 0.252 | 0.24 | 0.129 ±0.018 | 0.129 | 0.12 |

* Used as standard; concentrations given are selected by us from the recommended literature values and from the values of P.A. Baedecker.
**Recommended literature values
+Analysis by P.A. Baedecker

All the recommended literature values and the PAB values are kindly supplied by P.A. Baedecker of U.S. Geological Survey (Personal written communication, Nov. 1979).

## TABLE 3.

### CONCENTRATIONS (in ppm) OF REE IN KUANTAN DOLERITE DYKES OBTAINED BY INAA

| Element | QD-28A | QD-6 | QD-3 | QD-11 | QD-10 |
|---|---|---|---|---|---|
| La | 11.2 $\pm$ 0.3 | 11.4 $\pm$ 0.2 | 19.4 $\pm$ 0.4 | 20.1 $\pm$ 0.3 | 34.6 $\pm$ 0.3 |
| Ce | 21.4 $\pm$ 1.9 | 23.2 $\pm$ 0.8 | 40.4 $\pm$ 1.0 | 42.8 $\pm$ 2.0 | 78.2 $\pm$ 1.2 |
| Nd | 15.9 $\pm$ 1.5 | 17.5 $\pm$ 3.2 | 32.4 $\pm$ 1.9 | 31.3 $\pm$ 1.5 | 60.0 $\pm$ 1.1 |
| Sm | 3.55 $\pm$ 0.10 | 4.05 $\pm$ 0.02 | 5.76 $\pm$ 0.04 | 6.42 $\pm$ 0.08 | 10.1 $\pm$ 0.6 |
| Eu | 1.22 $\pm$ 0.05 | 1.06 $\pm$ 0.06 | 2.08 $\pm$ 0.12 | 2.36 $\pm$ 0.06 | 5.86 $\pm$ 0.06 |
| Gd | 3.5 $\pm$ 1.2 | N.D. | N.D. | 6.6 $\pm$ 1.9 | 12 $\pm$ 1 |
| Tb | 0.52 $\pm$ 0.04 | 0.67 $\pm$ 0.10 | 0.82 $\pm$ 0.17 | 0.81 $\pm$ 0.13 | 1.08 $\pm$ 0.09 |
| Yb | 1.78 $\pm$ 0.09 | 1.59 $\pm$ 0.10 | 2.23 $\pm$ 0.09 | 2.12 $\pm$ 0.30 | 2.46 $\pm$ 0.09 |
| Lu | 0.273 $\pm$ 0.012 | 0.205 $\pm$ 0.005 | 0.247 $\pm$ 0.026 | 0.247 $\pm$ 0.042 | 0.314 $\pm$ 0.032 |

N.D. means that the value is not determined.

from 8 to 11. They display fractionated REE patterns with distinct LREE (light rare earth elements) enrichment. The normalised La/Yb ratio varies from 4 to 9. The REE patterns of the Kuantan tholeiitic dykes are thus distinctly different from those of ocean floor and island arc tholeiites.

The most notable feature of the REE abundances in these dykes is the systematic increase of $\Sigma$REE with increasing differentiation. It is evident from Fig. 1 that the
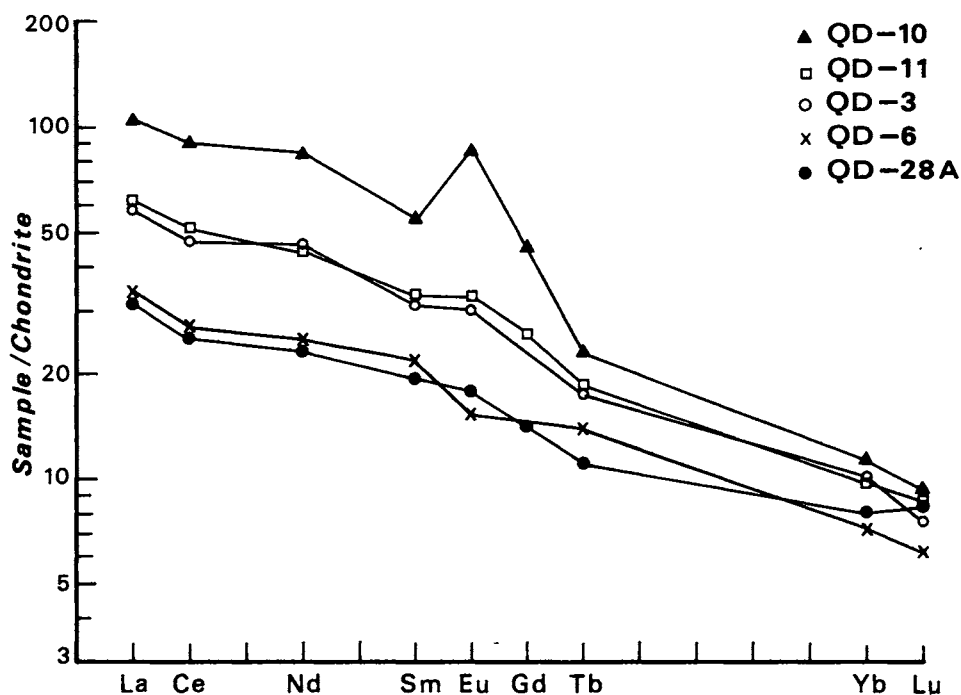


Fig. 1.   Chondrite-normalised REE abundances in five dolerite dykes from Kuantan.

absolute total REE concentration is the lowest in QD-28A which, on the basis of major element chemistry and petrography, has been identified as the least fractionated and close to the immediate parental magma composition. QD-28A has the lowest $FeO^*/(FeO^* + MgO)$ value amongst all the dykes analyzed for major elements. In contrast, QD-10 which is a highly differentiated rock having one of the highest $FeO^*/(FeO^* + MgO)$ values, shows the highest absolute $\Sigma REE$ concentration. The observed increase of REE concentration with increasing differentiation supports the general suggestion based on REE partition coefficients that during crystallization of a silicate melt the REE would be concentrated in the residual liquid (Haskin et al., 1971).

The REE distribution patterns show two other significant features. Firstly, it may be noted that there is a gradual development of positive Eu anomaly with advancing differentiation, QD-10 showing the highest anomaly (Fig. 1). Secondly, there is a systematic increase in the degree of LREE enrichment with increasing differentiation. The normalised La/Yb ratio increases from 4 in QD-28A to about 9 in QD-10. These features and the observed variation in the REE abundances, both absolute and relative, are explicable in terms of fractionation of clinopyroxene and olivine, and are consistent with the inferences drawn from petrographic and major element chemical studies. Detailed interpretative analysis of the REE abundance patterns as well as quantitative evaluation of the fractionation models based on REE and other trace and major elements are currently in progress.

## ACKNOWLEDGEMENT

## REFERENCES

BIGNELL, J.D. and SNELLING, N.J. (1977), Geochronology of Malayan granites. Overseas Geology and Mineral Resources, No. 47. Inst. Geol. Sciences, London.

BOWMAN, W.W. and MACMURDO, K.W. (1974). Radioactive decay gammas ordered by energy and nuclide. Atomic Data and Nuclear Data Tables, 13, 89–292.

CARDER, W., MAC MAHON, T.D. and EGAN, A. (1978). A radioisotope identification subroutine for use with gamma-ray spectrum analysis program SAMPO. Talanta, 25, 21–40.

FITCH, F.H. (1951). The geology and mineral resources of the neighbourhood of Kuantan, Pahang. Geol. Survey Dept., Federation of Malaya, Memoir 6 (New Series).

HANIF HUSSEIN, ABDUL (1975). The geology of the Kuantan area, with special reference to the petrology and chemistry of the basalts and dolerites. Unpublished B. Sc. (Hons) thesis, Dept. of Geology, University of Malaya.

HASKIN, L.A., HELMKE, P.A., PASTER, T.P. and ALLEN, R.O. (1971). Rare earths in meteorite, terrestrial and lunar matter. In A.O. Brunfelt and E. Steinnes (Ed.): Activation analysis in geochemistry and cosmochemistry. Universitetsforlaget, Oslo, 201–218.

SITA RAM, G. (1979). Instrumental neutron activation analysis of Malaysian offshore carbonate samples irradiated in a nuclear reactor. Sains Malaysiana, 8, 67–80.

SITA RAM, G. and GANGADHARAM, E.V. (1978). Activation analysis using isotopic neutron source and high-resolution gamma-ray spectrometry. J. Singapore Nat. Acad. Sci., 7, 95–103.